

BRIEF COMMUNICATION

Interaction of 8-Hydroxyquinoline with Cadmium Halides in Solid State

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The solid state reactions of 8-hydroxyquinoline (8-HQ) and cadmium halides (CdX_2 ; $X = Cl, Br, \text{ and } I$) have been studied. Each reaction follows the rate equation $X^n = kt$. The activation energies calculated from the progress of the reaction studied by the lateral diffusion technique are 74.55 ± 1.22 , 84.65 ± 3.88 , and 101.66 ± 0.93 kJ mole^{-1} for $CdCl_2$ -8-HQ, $CdBr_2$ -8-HQ and CdI_2 -8-HQ reactions, respectively. 8-HQ diffuses into cadmium halide grains by a defect mechanism; penetration to the grains is preceded by surface migration. The reactions were followed by chemical analysis, IR spectral studies, and thermal and conductivity measurements. A single addition product, $[CdX_2 \cdot (8-HQ)]$, was obtained for $CdCl_2$ and $CdBr_2$, whereas CdI_2 gave rise to two addition products, $CdI_2 \cdot (8-HQ)$ and $CdI_2 \cdot (8-HQ)_2$. © 1995 Academic Press, Inc.

INTRODUCTION

8-HQ, which forms highly stable chelates in solution (1), appears to have a strong chelating action in the solid state as well. Despite the increased attention that has been paid to the study of solid state reactions in recent years, it remains confined to mostly inorganic-inorganic or organic-organic processes; references to inorganic-organic systems are few. In continuation of our work (2), this paper reports the kinetics and mechanism of the solid state interaction of 8-HQ with cadmium halides.

EXPERIMENTAL

Materials. BDH reagent grade $CdCl_2$ and $CdBr_2$, Analaar grade CdI_2 (Glaxo Laboratories Ltd., India, and 8-HQ (Aldrich Chemical Company, Inc., melting point 74.9°C) were used without further purification. The reactants were powdered and sieved to above 300 mesh size.

Kinetic measurements. The reaction products were colored and the progress of the reaction was followed by

the lateral diffusion technique (3). The isothermal growth of the product layer at the interface was recorded at different time intervals and also at different temperatures by a traveling microscope having a calibrated scale in its eye-piece (least count 0.001 cm). The reactants were placed over one another in a vertical Pyrex glass tube of uniform bore. The reaction tube was kept in an air thermostat controlled to $\pm 0.5^\circ\text{C}$. One gram of each reactant (300 mesh) was taken each time and pressed to identical pressure as reported earlier (4).

A gap developed at the interface between the product boundary and 8-HQ with a plane surface on the product side and a convex surface on the 8-HQ side. Later, lateral diffusion experiments were run, keeping air gaps of different lengths between the reactants at 60°C . The reactions proceeded exactly alike, giving similar products on the CdX_2 side. The reaction rate decreased with increasing length of the air gap.

Product analysis. The colored products were separated manually by breaking the reaction tubes. Reactants in the solid state were also mixed in a 1 : 1 molar ratio and heated to 60°C for 10 days. In another experiment, solid CdX_2 was mixed with a large excess of 8-HQ (above 3 mole) and heated to 60°C for the same duration. During the process the mixtures were repeatedly pulverized and mixed. The products obtained in the last case were washed repeatedly with acetone to remove the unreacted 8-HQ. The products so obtained were dried and the metal content for all the sets was estimated gravimetrically (5). Nitrogen, carbon, and hydrogen were estimated by a microanalytical technique.

Thermal studies. CdX_2 and 8-HQ (all above 300 mesh size) were weighed separately, mixed thoroughly in 1 : 1 and 1 : 2 molar ratios, poured immediately into a Dewar flask, completely insulated and maintained at a

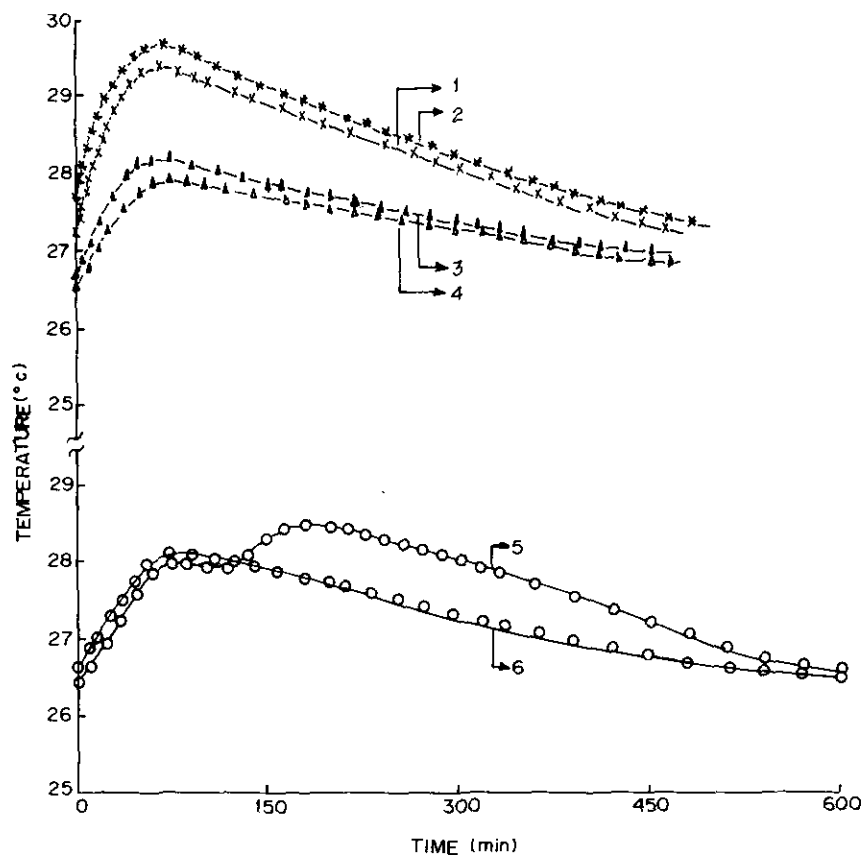


FIG. 1. Variation in temperature with time. (1) CdCl_2 :8-HQ (1:2); (2) CdCl_2 :8-HQ (1:1); (3) CdBr_2 :8-HQ (1:1); (4) CdBr_2 :8-HQ (1:2); (5) CdI_2 :8-HQ (1:2); (6) CdI_2 :8-HQ (1:1).

fixed temperature. The rise in temperature as a function of time was recorded using a Beckman thermometer calibrated to 0.01°C . The plots of temperature against time are shown in Fig. 1.

Electrical conductivity measurements. Electrical conductivity measurements were made with a Teflon conductivity cell (self designed) on a powdered reaction mixture compressed into a disk. CdX_2 and 8-HQ (molar ratios 1:1 and 1:2) were mixed thoroughly, placed immediately into a die, and pressed into a disk of 0.31 cm^2 surface area and 0.3 cm thickness. The disk was held between platinum electrodes with the same surface area and the change in conductivity with time was measured by a Gen Rad 1657 Model RLC digibridge at a frequency of 120 Hz . Results are depicted in Fig. 2.

IR studies. Infrared spectra of the reaction products and 8-HQ were taken in KBr disks with a Beckman IR-120 spectrophotometer. Important infrared spectral bands are given in Table 1.

RESULTS AND DISCUSSION

Chemical interaction. Results of chemical analyses of the products (compared with calculated ones) show

that CdCl_2 and CdBr_2 react with 8-HQ in only a 1:1 ratio whereas CdI_2 reacts in both 1:1 and 1:2 molar ratios. As soon as CdI_2 and 8-HQ were mixed and ground in a mortar at room temperature, a cream colored product was formed which turned orange in the case of the 1:2 molar mixture. No evidence was obtained for the evolution of hydrogen halides during the reaction. IR spectra of the products obtained (i) by mixing CdI_2 with excess 8-HQ (more than 2 molar) and removing the unreacted 8-HQ by washing it with chloroform and (ii) by mixing CdI_2 with 8-HQ in 1:2 molar ratio are the same. The IR spectra of 1:1 molar mixture of CdI_2 and 8-HQ were different from those of (i) and (ii).

Chemical analysis revealed that CdCl_2 and CdBr_2 react with 8-HQ in a 1:1 molar ratio only. IR spectra of the product obtained (i) by mixing CdCl_2 or CdBr_2 with 8-HQ in 1:2 molar ratio and removing the unreacted 8-HQ by washing with chloroform and (ii) by mixing CdCl_2 or CdBr_2 with 8-HQ in a 1:1 molar ratio are the same. Elemental analyses of the reaction products also indicate that CdCl_2 and CdBr_2 react only in a 1:1 molar ratio, whereas CdI_2 reacts in 1:1 and 1:2 molar ratios.

Thermal (Fig. 1) and conductance (Fig. 2) measurements also show that cubic CdCl_2 and CdBr_2 give only a

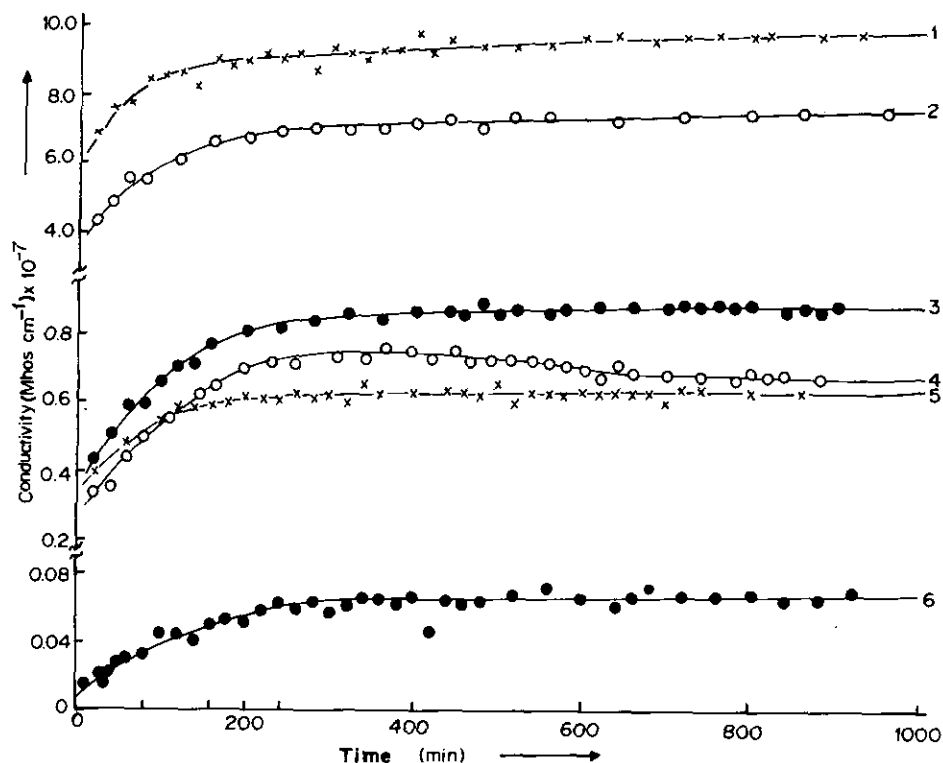


FIG. 2. Variation of electrical conductivity with time. (1) CdCl_2 and 8-HQ (1:1); (2) CdI_2 and 8-HQ (1:1); (3) CdBr_2 and 8-HQ (1:1); (4) CdI_2 and 8-HQ (1:2); (5) CdI_2 and 8-HQ (1:2); (6) CdBr_2 and 8-HQ (1:2).

1:1 adduct, whereas hexagonal CdI_2 gives a 1:1 adduct in a 1:1 molar mixture which with additional 8-HQ changes into the 1:2 complex.

The vibrational spectra (Table 1) of the reaction products CdI_2 -8-HQ (1:1), CdI_2 -(8-HQ)₂ (1:2), CdBr_2 -8-HQ

(1:1), and CdCl_2 -8-HQ (1:1) are quite informative and provide unambiguous clues regarding the mode of coordination of the ligand. The aromatic ring vibrations coupled with the pyridyl ring vibrations are in general positively shifted in the complex compared to those of the free li-

TABLE 1
IR Spectra

Compound	Wavenumber (cm^{-1})					
	OH	Ring vibration	C-O-H	M-O	M-N	M-X
8-HQ	3660 (bs)	1590 (s) 1595 (s) 1465 (s)	1260 (s)	—	—	—
CdI_2 -(8-HQ) 1:1 product	3760 (b)	1650 (m) 1520 (s) 1455 (vs)	1220	555 (m)	360 (m)	—
CdI_2 -(8-HQ) ₂ 1:2 product	3640 (b)	1615 (s) 1500 (s) 1485 (s)	1260 (s)	—	370 (w)	—
CdBr_2 -(8-HQ) 1:1 product	3735 (b)	1635 (s) 1560 (s) 1455 (s)	1225 (m)	550 (m)	365 (w)	—
CdCl_2 -(8-HQ) 1:1 product	3740 (b)	1620 (m) 1540 (s) 1460 (s)	1230 (m)	555 (m)	370 (w)	280 (s)

gand, indicating the pyridyl nitrogen coordination. The C–O–H stretching vibration, as expected, is negatively shifted due to the coordination of the phenolic group. However, in $\text{CdI}_2\text{--}(8\text{-HQ})_2$, the C–O–H stretching vibration remains unaffected, suggesting its noninvolvement in the coordination. The metal ligand stretching vibrations for M–O and M–N are observed at the reported position (6). The Cd–Cl stretching vibration has been observed as a strong band at 280 cm^{-1} , while Cd–I and Cd–Br stretching vibrations could not be recorded, as these fall at about 150 and 190 cm^{-1} , respectively, which is beyond the range of our instrument.

Lateral diffusion. In lateral diffusion experiments, the product boundary that formed at the interface grew only on the CdX_2 side. This shows that 8-HQ is the diffusing species. The isothermal kinetic data best fit the equation

$$X^n = kt,$$

where X is the thickness of the product formed at time t , k , and n are constants. The gradual rise in k with a rise in temperature suggests that the process is diffusion-controlled (4, 7). The k values show the Arrhenius dependence. The activation energies for the formation of $\text{CdCl}_2\text{--}8\text{-HQ}$, $\text{CdBr}_2\text{--}8\text{-HQ}$, and $\text{CdI}_2\text{--}(8\text{-HQ})_2$ are re-

spectively 74.55 ± 1.2 , 84.61 ± 3.88 , and $101.66 \pm 0.93\text{ kJ mole}^{-1}$. These high values suggest that diffusion in cadmium halides is by defect mechanism.

The simultaneous development of a gradually increasing gap between the colored product and 8-HQ suggests that 8-HQ might be reacting with CdX_2 via vapor phase. Experiments with initial air gaps of different lengths between the reactants proceeded in a similar manner. It is interesting to note that the gap had a plane surface on the product side and a convex surface on the 8-HQ side, which suggests that diffusion of 8-HQ is via the surface and not the vapor phase.

X-ray diffractograms showed the products to be non-crystalline.

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