

### 13.3 \*The Factor that Determines Photo-induced Crystalline-state Reaction

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**Abstract** The photo-induced crystalline-state reaction of cobaloxime complexes were investigated by X-ray diffraction method. The reactivity or the reaction rate is dependent only on the volume of the reaction cavity. The hydrogen bond formation of the reactive group and the difference of the base ligand have no effect.

#### INTRODUCTION

Solid-state reaction is very useful to obtain functional materials, for example asymmetric compounds or crystalline polymers, that cannot be obtained from solutions. Among the solid-state reactions, crystalline-state reaction of cobaloxime complexes are very outstanding because the reaction proceeds without degradation of the single crystal form.

It has been found that the chiral 1-cyanoethyl group bonded to the cobalt atom in the crystal of cobaloxime complex is racemized by exposure to visible light keeping the single crystal form (Ohashi and Sasada, 1977). Figure 1 shows a cobaloxime complex with (*S*)-1-phenylethylamine as axial ligand. The cobalt atom is surrounded by the dimethylglyoxime plane, a chiral cyanoethyl group, and the base ligand. If this crystal is irradiated by light, the chiral cyanoethyl group changes its configuration to the disordered racemate, that is (*R*)- and (*S*)-cyanoethyl groups are distributed randomly in the crystal, both of the cyanoethyl groups are superimposed in Fig. 1. For various base ligands, various reactions have been observed. These reactions are initiated by the Co-C bond cleavage (Ohashi, Yanagi, Kurihara, Sasada, and Ohgo, 1981). In this study the relationships between the reactivity or the reaction rate and the packing of the reactive group were investigated for some cobaloxime complexes with various amines or phosphines as axial base ligands by X-ray diffraction method, and was examined what is the responsible factor for the crystalline-state photo-reaction.

#### EXPERIMENTAL

The various cobaloxime crystals, pyrrolidine (pyrr), (*S*)-phenylethylamine (pea), and dimethylphenylphosphine (dmpp) as axial ligands with (*R*)-1-cyanoethyl group, and pea with (*S*)-1-cyanoethyl group (S-pea), were prepared. The integrated intensities of diffracted X-rays were measured using four-circle diffractometer. Based on the intensity data, the crystal structures were determined. The changes of cell dimensions with exposure time were also measured continuously using four-circle diffractometer.

## RESULTS and DISCUSSION

The variation in cell dimensions for pyrr were shown in Fig. 2. It indicates that the variation follows first-order kinetics. The reaction rates were calculated by least-squares fitting procedure. The values are shown in Table 1.

It has been proposed that the packing around the cyanoethyl group plays an important role in crystalline-state reaction. The reaction cavity was defined in order to estimate the packing of the reactive group more precisely (Ohashi, *et al.*, 1981); the space limited by a concave surface of the surrounding atoms around the reactive group in the crystal, the radius of each sphere is taken to be 1.2 Å greater than the van der Waals radius of the corresponding atom (Fig. 3). The cavity of pyrr is shown in Fig. 4.

In order to investigate the relationship between the reactivity or the reaction rate and the packing of the reactive group, the nine cobaloxime complexes were compared; diethylphenylphosphine (depp; Tomotake, Uchida, Ohashi, Sasada, Ohgo, and Baba, 1984), diphenylethylphosphine (dpep; Tomotake, *et al.*, 1984), tributylphosphine (tbp; Kurihara, Uchida, Ohashi, Sasada, Ohgo, and Baba, 1983), triphenylphosphine (tpp; Kurihara, *et al.*, 1983), pyrr, S-pea, pea, and dmpp, of which S-pea has two polymorphs. Of these nine cobaloxime complexes, tpp, pyrr, and one of the S-pea crystals have hydrogen bonds between the N atom in the cyanoethyl groups and the solvent water molecules. The volume of the reaction cavity and the reaction rate are shown in Table 1.

Comparing the various cobaloxime complexes, it found that the reactivity and the reaction rate were dependent only on the volume of the reaction cavity, other factors, for example hydrogen bond formation between reactive group and the surrounding atom, could be neglected. There are no exceptions on this rule. Furthermore, the volume of the reaction cavity required to carry out the reaction can be determined to be 11.5 Å<sup>3</sup>. This value, 11.5 Å<sup>3</sup>, is appreciable to all of the crystalline-state reactions of cobaloxime complexes with cyanoethyl groups (Takenaka, Arisawa, and Ohashi, 1995).

This fact is contrast to the solid-state photo-isomerization of 2-cyanoethyl group in cobaloxime complex. If the cobaloxime complex with β-cyanoethyl group is irradiated by light in solid-state, isomerization of cyanoethyl group is observed (Fig. 5). In that case, if the cyanoethyl group has N-HO hydrogen bond with water molecule, the reaction is accelerated compared to the crystal without the hydrogen bond. This acceleration was attributed to the stabilization of the β-cyanoethyl radical to the α-radical by the hydrogen bond (Sekine and Ohashi, 1991). But in the case of racemization, the created α-cyanoethyl radical is already stable. The unpaired electron does not transfer to any other atom in radical. Furthermore, because the methyl group in cyanoethyl group moves most drastically in crystalline-state racemization, the hydrogen bond is not an obstacle of the inversion of the cyanoethyl group. So the hydrogen bond has no effect in racemization.

## CONCLUSIONS

The crystal is constructed in the consequence of the equilibrium of many forces, for example electrostatic force, or van der Waals force, and so on. But in the case of crystalline-state racemization of cobaloxime complex with cyanoethyl group, the reaction proceeds dependent only on the packing of the reactive group. Although the number of cyanoethyl radical created by the cleavage of the Co-C bond may differ according to the base ligand or the hydrogen bond formation between the reactive group, these effects are found to be negligible. It can be concluded that the packing of the reactive group is responsible factor for photo-induced crystalline-state reaction.

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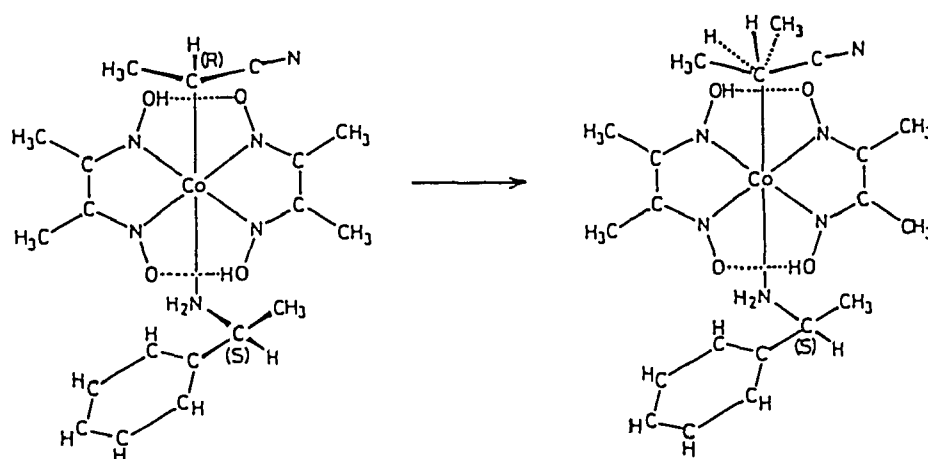


Figure 1 Crystalline-state racemization of cobaloxime complex,  $[(R)\text{-}1\text{-cyanoethyl}][(\text{S})\text{-phenylethylamine}]\text{cobaloxime}$  (Ohashi and Sasada, 1977).

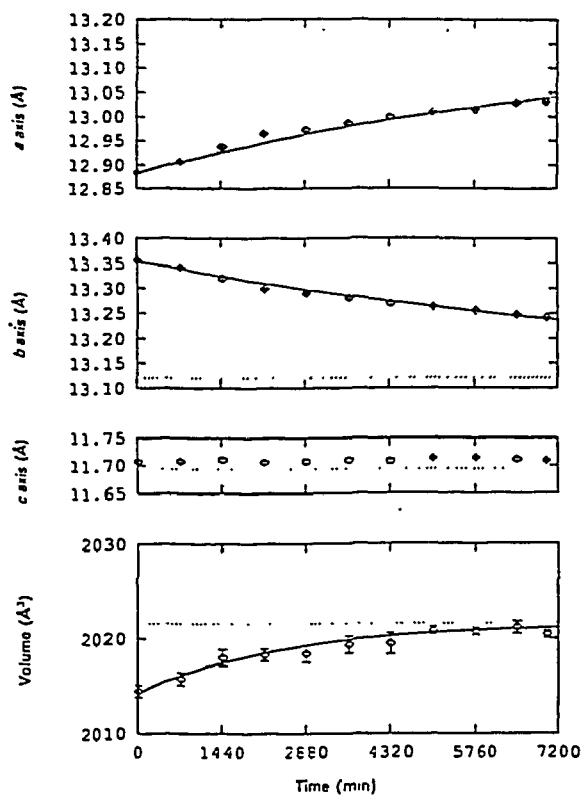


Figure 2 Change of the unit cell dimensions on exposure time. Solid curves represent the first-order kinetics and dotted lines indicate the final parameters.

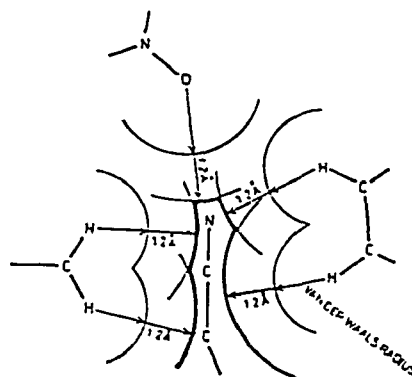


Figure 3 The definition of the reaction cavity (Ohashi, *et al*, 1981).

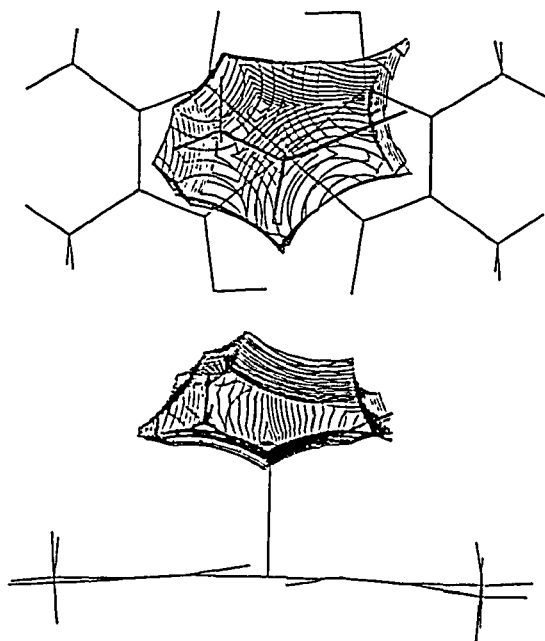


Figure 4 The reaction cavity of [(*R*)-1-cyanoethyl](pyrrolidine)cobaloxime projected onto the cobaloxime plane and the side view. Contours are drawn in sections separated by 0.1 Å.

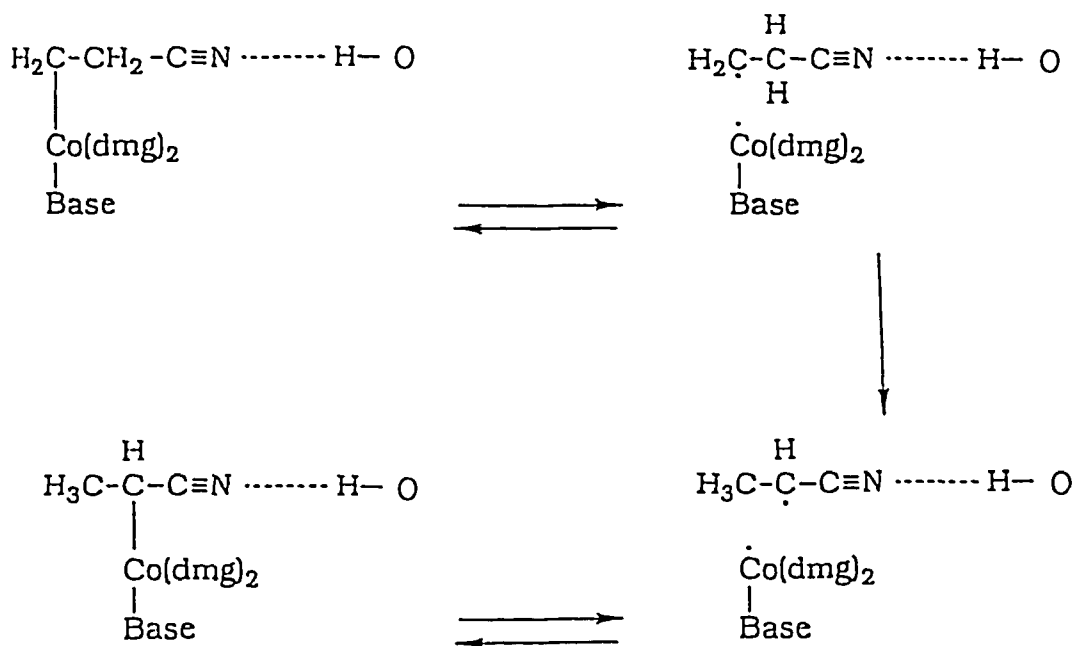


Figure 5 The  $\beta$ - $\alpha$  photo-isomerization of cobaloxime complex (Sekine and Ohashi, 1991).

Table 1 The size of the reaction cavity and the reaction rate.

	$V_{cav}$ ( $\text{\AA}^3$ )	reaction rate ( $\times 10^{-6} \text{s}^{-1}$ )
depp	8.4	-†
S-pea(II)	8.6	-
dpep	10.2	-
tbp	10.6	-
tpp	11.3	-
pyrr	11.6	1.69
S-pea(I)	12.8	2.38
pea	15.3	3.13
dmpp	18.0	4.80‡

†: Racemization was not observed at room temperature.

‡: The value determined from the site occupancy factor of the cyanoethyl group.