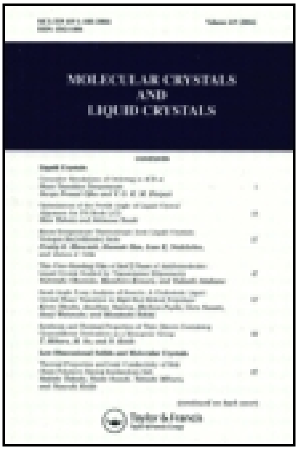

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Three Factors Controlling the Reaction Rate in Solid State Photoisomerization

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THREE FACTORS CONTROLLING THE REACTION RATE IN SOLID STATE PHOTOISOMERIZATION

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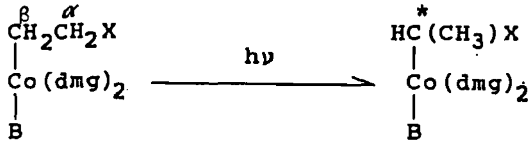
Abstract Through comparison of the reaction rates in solid-state photoisomerization in several related cobaloxime complex crystals with the cavities for the reactive group, the reaction rate has been found to be affected by three factors; the size of the cavity, the conformation of the reactive group and the hydrogen bond of the reactive group with the neighboring molecule.

INTRODUCTION

We have found that the chiral groups bonded to the cobalt atom in cobaloxime complex crystals are racemized without degradation of crystallinity. The rate of racemization is so slow that several intermediate structures can be obtained by X-ray analyses. Various reaction pathways and the rates have been observed in this racemization process from the structures at several intermediate stages. We have defined the reaction cavity for the chiral group, which explained well the differences in the reaction mechanism.[1]

Recently it was found that the alkyl groups bonded to the cobalt atom in the cobaloxime complex crystals were isomerized on exposure to visible light, as shown in the Scheme.[2] The reaction occurred only in the solid state and the crystal was usually decomposed as the



B: base ligand, X: CN,COOCH$_3$

SCHEME β-α Photoisomerization of cobaloxime complex

reaction proceeded. This finding has stimulated us to further investigation whether or not the relation between the reactivity and the cavity size holds good for the solid state isomerization, although the crystallinity was not kept intact during photoreaction.

ISOMERIZATION RATE

When the reactive group is a β-cyanoethyl group, the rate of the isomerization is estimated from the IR spectra. A KBr disc of the cobaloxime complex was irradiated with a Xenon lamp and the IR spectra were measured at constant intervals. The spectra due to the stretching vibration mode of the cyano group gradually changed from 2250 cm^{-1} to 2200 cm^{-1}. The reaction rate was obtained from decrease of the cyano spectrum of the β-cyanoethyl group and an increase of the spectrum of the α-cyanoethyl group.

FIRST FACTOR(CAVITY SIZE)

Two crystal forms were obtained under the same conditions when the base ligand was 3-methylpyridine.[3] The molecular structures of the I and II forms are shown in Figure 1(a). The β-cyanoethyl group of the form I takes an ordered structure while the structure of the form II is a disordered one. The rate of the isomerization is shown in Figure 1(b). The crystal of the form II revealed

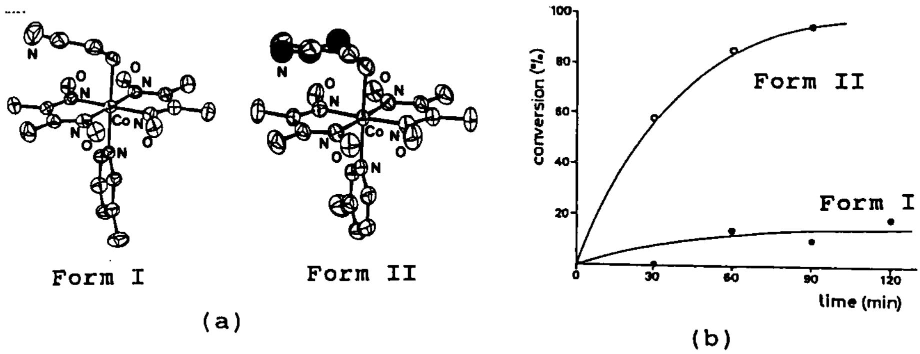
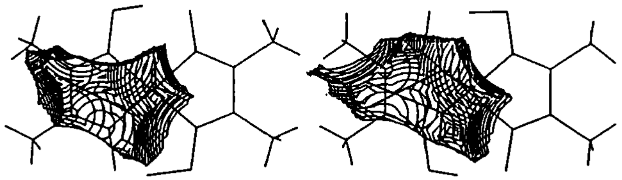


FIGURE 1 (a)Molecular structures and (b)reaction rates of two crystal forms.

a significantly greater rate than that of the form I. The conversion values of II and I are about 100% and 20%, respectively.

In order to estimate the void space around the reactive group in the crystal structure, the reaction cavity for the β-cyanoethyl group was drawn for each crystal. Figure 2 shows the cavities the two crystal forms. The volumes of the cavities of the I and II forms were calculated to be 10.36 $A^3$and 11.88 A^3, respectively. It is clear that the β-cyanoethyl group with greater cavity has larger reaction rate than that with smaller cavity. This is the first factor controlling the



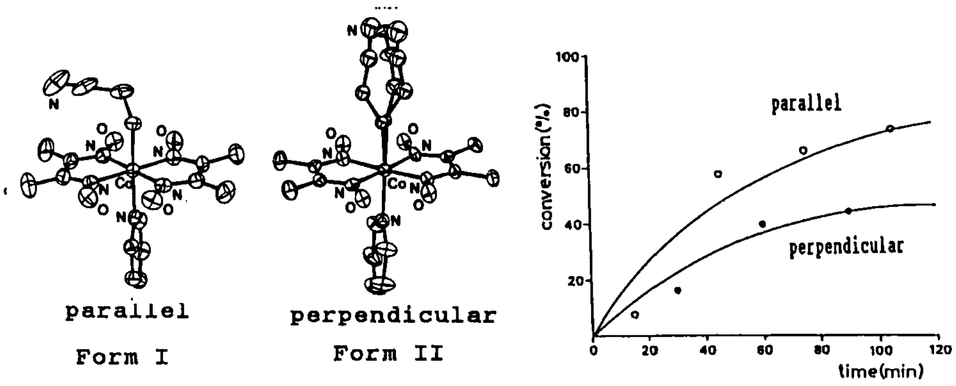
Form I Form II

FIGURE 2 Cavities for the β-cyanoethyl group viewed along the normal to the cobaloxime plane. Contours are drawn in sections separated by 0.1A.

reaction rate in this photoisomerization. The same result has been obtained for the crystalline-state racemization by X-ray exposure.

SECOND FACTOR(CONFORMATION)

The next example is the cobaloxime complex with pyridine as an axial base ligand. Two crystal forms were also obtained under similar conditions.[4] The conformations of the β-cyanoethyl groups were different in the two crystal forms as shown in Figure 3(a). The β-cyanoethyl group of the form I has an approximately parallel conformation to the cobaloxime plane while that of the form II takes a perpendicular conformation to the cobaloxime plane. Moreover, β-cyanoethyl group of the form II has a disordered structure. The cavities for β-cyanoethyl group in the two crystal forms were drawn and the volumes were calculated to be 10.51 $Å^3$ and 12.31 $Å^3$, respectively.



(a) (b)

FIGURE 3 (a)Molecular structures and (b)reaction of two crystal forms.

Although the reaction cavity of the form I is significantly smaller than that of the form II, the reaction rate of the form I is clearly faster than that of the form II as shown in Figure 3(b). This is well explained from a topochemical point of view. The β-cyanoethyl group with parallel conformation is more easily transformed to the α-cyanoethyl group than that of the perpendicular conformation, because the displacement of the atoms of the parallel conformations should be smaller than that of the perpendicular one as shown in Figure 4. The second factor seems to be more important than the first factor.

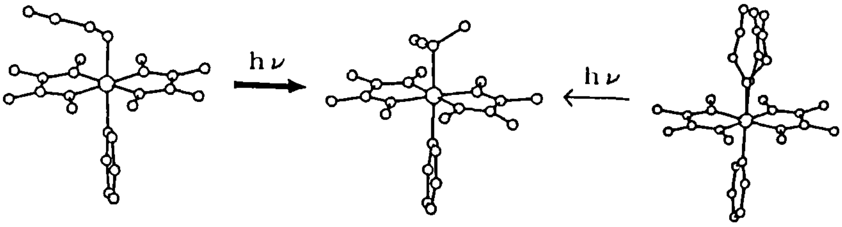
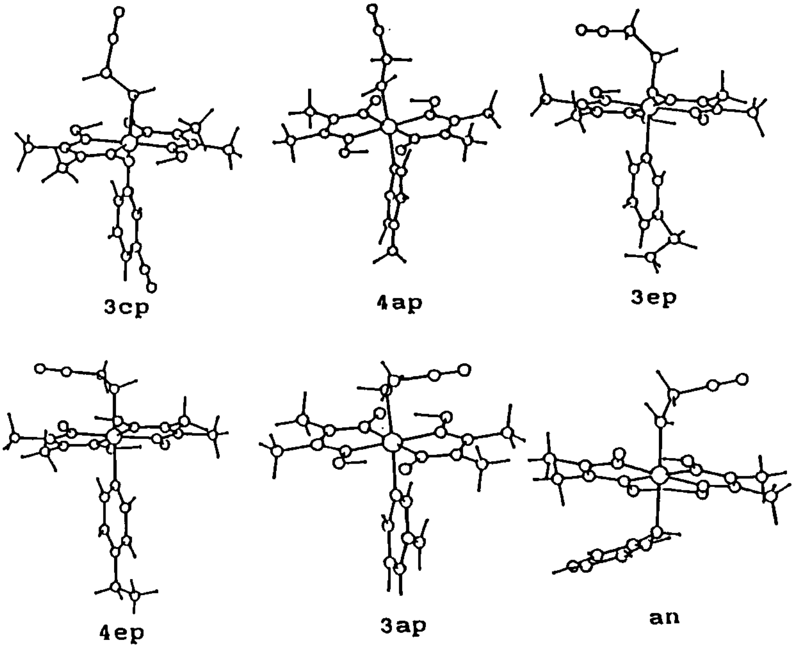


FIGURE 4 Structural change in the photoisomerization

THIRD FACTOR(HYDROGEN BOND)

In order to examine the factors more quantitatively, six cobaloxime crystals with different axial base ligands were examined.[5] They have 3-cyanopyridine (3cp), 4-aminopyridine (4ap), 3-ethylpyridine (3ep), 4-ethylpyridine (4ep), 3-aminopyridine (3ap) and aniline (an), the molecular structures of which are shown in Figure 5. The β-cyanoethyl groups of 3cp and 4ap complexes have a perpendicular conformation while those of 3ep, 4ep, 3ap and an are parallel. The rate of the isomerization at early stages, within 40 minutes, follow first-order kinetics, as shown in Figure 6. The rate constants were calculated by least-squares fitting. Table 1 gives the rate constants and volumes of the cavities for six crystals. It is clear that the rate constants of the crystals with parallel conformation are significantly greater than those with perpendicular



3cp 4ap 3ep

4ep 3ap an

FIGURE 5 Molecular structures of six cobaloxime complexes

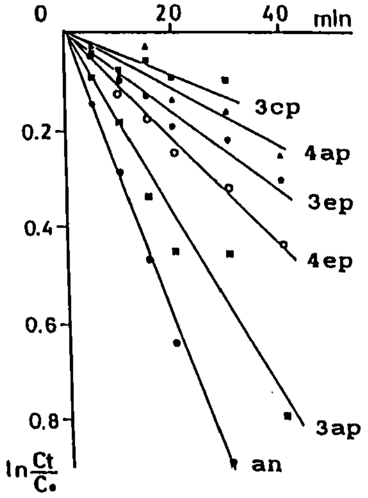


FIGURE 6 Isomerization rates at early stages. The solid lines are obtained by least-squares fitting.

TABLE I Relation between the volume of the cavity(A^3) and the rate constant($10^{-4}s^{-1}$).

complex	volume	rate const.	conformation
3cp	12.24	0.8	perpendicular
4ap	14.99	1.1	perpendicular
3ep	13.12	1.4	parallel
4ep	14.00	1.6	parallel
3ap	10.06	3.2	parallel
an	14.97	4.2	parallel

conformation. Moreover, the 4ap crystal, with a greater cavity than 3cp, shows the greater rate constant.

For the crystals with parallel conformation, there appears no relation between the size of the cavity and the reaction rate. Although the cavity of the 3ap crystal is the smallest, the rate constant is greater than those of the 3et and 4et crystals. The rate constant of the an crystal seems to be too large considering its cavity size. These facts clearly indicate that another factor should be taken into account.

In the 3ap and an crystals, the nitrogen atoms of the β-cyanoethyl groups are hydrogen bonded to the amino groups of the neighboring molecules, whereas such a hydrogen bond is not observed in the other four crystals. The hydrogen bond is schematically shown in Figure 7.

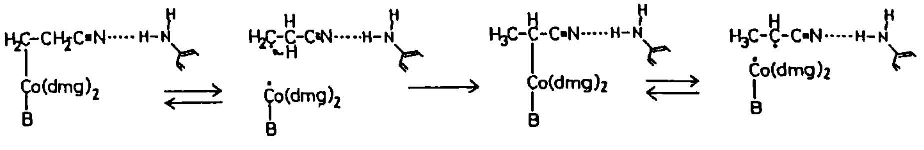


FIGURE 7 Role of the hydrogen bond in the photoisomerization

When the Co-C bond is cleaved by visible light, the β-cyanoethyl radical will be produced. Since the radical is unstable, most of the radicals would return to the original β-cyanoethyl group. A small part of the radicals may be transformed to the α-cyanoethyl radical and then the complex with the α-cyanoethyl group will be produced in this photoisomerization. The rate determining step should be the β-α radical transformation. If the nitrogen atom of the β-cyanoethyl group is hydrogen bonded to the amino group of the neighboring molecule, the β-cyanoethyl radical should be stabilized and the extent of β-α radical transformation should increase. This causes the greater reaction rate when the β-cyanoethyl group is hydrogen bonded. This is the third factor. It must be emphasized that the third factor cannot be recognized without the idea of the reaction cavity. Although the structure in which the β-cyanoethyl group with perpendicular conformation is hydrogen bonded with the neighboring molecule has not been observed yet, the third factor seems to be most important among the three factors, considering the significantly greater rate of the 3ap and an crystals.

ACKNOWLEDGMENT

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