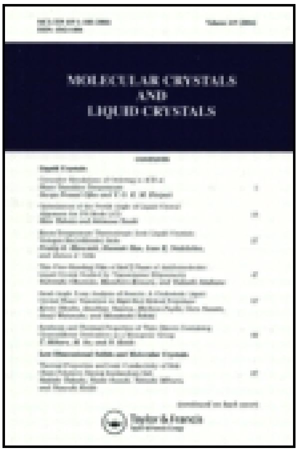

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MECHANISM OF SOLID-STATE RACEMIZATION FOR OPTICALLY ACTIVE ALKYL COBALOXIME COMPLEXES —— SYNTHESIS AND SOLID-STATE REACTION OF DEUTERIUM-LABELED COMPLEXES

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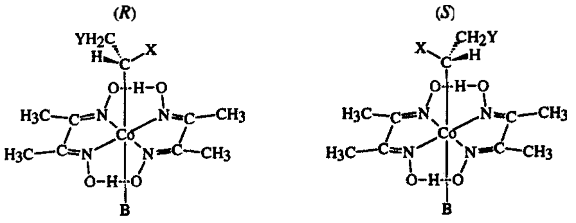
Abstract

The deutelium-labeled chiral 1,2-disubstituted ethyl cobaloxime complexes were synthesized, and the rate constants of the solid-state photoracemization and photoisomerization of these complexes were determined . The reaction mechanism for the solid-state photoracemization was elucidated by rationalization of these results.

INTRODUCTION

We previously reported that optically active 1-substituted ethyl cobaloximes and 1,2-disubstituted ethyl cobaloximes coordinated with various axial ligands racemized on irradiation of visible-light in the solid-state 1). The rate of the racemization was found to be controlled by (1) the volume of the cavity for the reactive group, (2) intermolecular interaction, and (3) flexibility around the reactive group 1),2). However, the reaction mechanism is not clear.



Substituents of alkyl groups
- 1 X=CN,Y=H
- 2 X=COOMe,Y=H
- 3 X=COOMe,Y=COOMe
- 4 X=COOEt,Y=COOEt
- 5 X=COOAllyl,Y=COOAllyl

Axial base
- B=pyridines, phosphines and amines

FIGURE 1 Structures of Optically Active Cobaloxime Complexes

In order to elucidate the mechanism for the racemization of optically active alkyl cobaloximes, we synthesized deuterium-labeled (D-labeled) complexes and examined their photoracemization and photoisomerization.

RESULTS AND DISCUSSION

Three possible pathways (a), (b), and (c) are considered for the racemization reaction (FIGURE 2): (1) the first proceeds via 180° out-of-plane rotation of the radical produced by photohomolysis of the Co-C bond followed by the recombination [path (a)]; (2) the second involves 180° out-of-plane rotation of the olefin formed by H-atom abstraction from the initially formed alkyl radical species [path (b)]; and (3) the third is possible for symmetrically 1,2-disubstituted ethyl complexes.

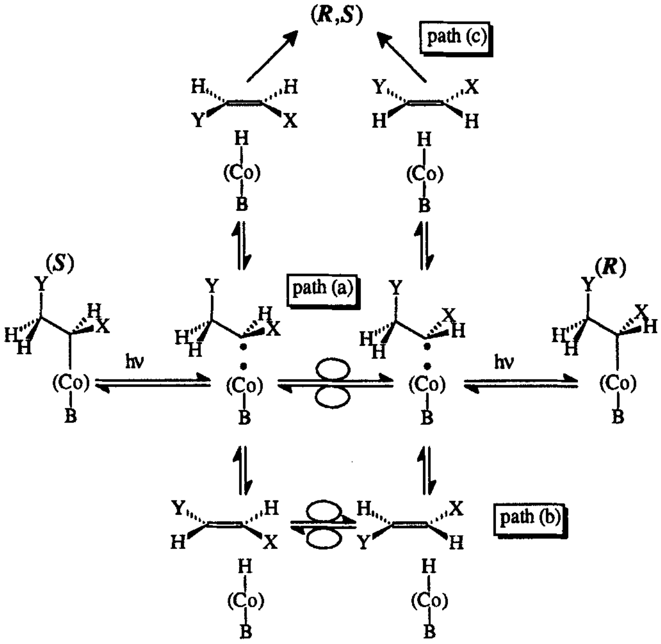


FIGURE 2 Reaction mechanism of the solid-state racemization for alkyl cobaloximes

Abstraction of hydrogen on the carbon(2) adjacent to the free radical by Co(II) species gives (*E*)- and (*Z*)-olefins, and an incidental attack of H-atom of hydride complex to either carbon (1) or (2) of (*Z*)-olefin can afford to racemate without a 180° out-of-plane rotation of the radical or olefin [path (c)].

In order to clarify which pathway racemization of each substrate proceeds through, first we attempted to detect olefins by ^{1}H-NMR measurement. Signals due to acrylonitrile were not detected in all the NMR spectra of the irradiated samples of the 1-cyanoethyl complexes , (*R*)-1. On the other hand, signals due to olefins were observed in the NMR spectra of the irradiated samples of 1-(methoxycarbonyl)ethyl , 1,2-di(methoxycarbonyl)ethyl , 1,2-di(ethoxycarbonyl)ethyl , and 1,2-di(allyloxycarbonyl)ethyl complexes [(*R*)-2, (*R*)-3, (*R*)-4 and (*S*)-5]. However, there is not necessarily correlation between the racemization rate and the time for the olefin to be detected.

The results show that (*R*)-1 racemizes through path (a), and racemization for (*R*)-2, (*R*)-3, (*R*)-4 and (*R*)-5 may involve path (b) or path (c) to some extent, but it is not clear whether the racemization through olefin is the major path.

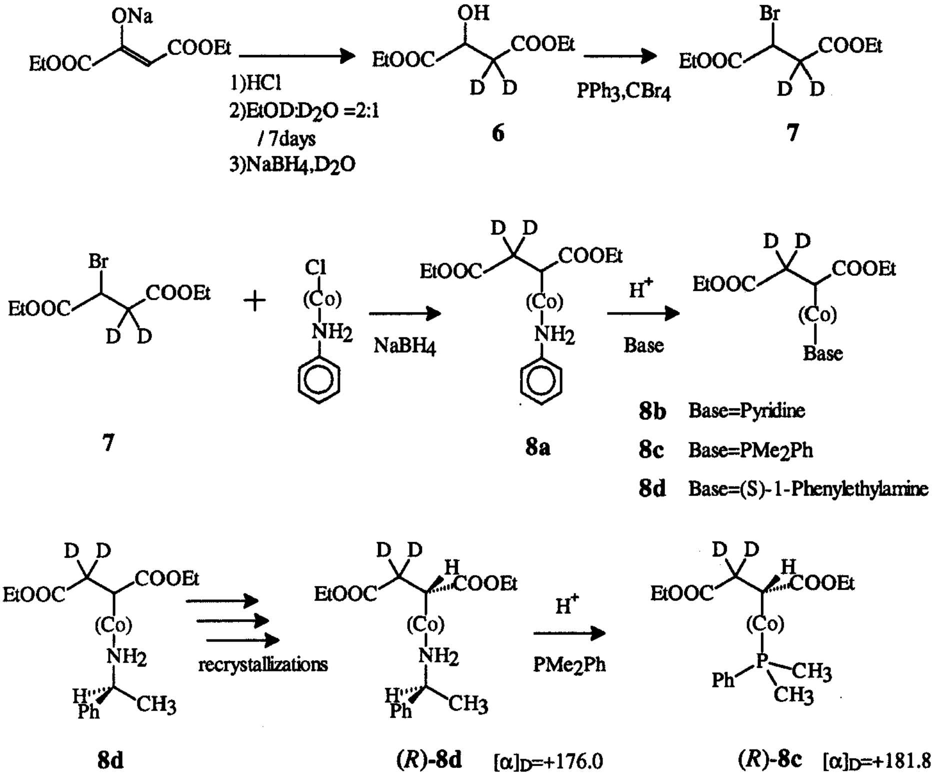


FIGURE 3 Synthesis of deuterium-labeled complexes

Further, path (c) requires formation of (*Z*)-olefin, but the geometry of the detected olefins is almost (*E*). These results urged us to examine whether 1,2-isomerization occurred or not, and ,if occurred, to meassure the isomerization rate.

For this purpose, D-labeled complexes were synthesized and solid-state photoreactions of these complexes were examined. 2,2-Dideuterio-1,2-di(ethoxycarbonyl)ethyl complexes , **8b**, **8c**, (*R*)-**8c** and (*R*)-**8d**, were synthesized by the reaction of bis(dimethylglyoximato)cobalt(I) anion with diethyl 1-bromo-2,2-dideuteriosuccinate produced from reduction of diethyl 2,2-dideuteriooxaloacetate followed by the bromination and axial ligand displacement (FIGURE 3). Further, D-labeled optically active cobaloxime complexes were obtained by recrystallizations of (*S*)-1-phenylethylamine-coordinated 2,2-dideuterio- 1,2-di(ethoxycarbonyl)ethyl complex followed by axial ligand displacement.

If 1,2-isomerization occurs, **8** should afford 1,2-dideuterio-1,2-di(ethoxycarbonyl)ethyl complex, and hydrogen content at carbon(1) should decrease. Consequently, we can estimate the isomerization rates by ^{1}H- and ^{13}C-NMR spectra of the photo-irradiated sample. The isomerization rates for D-labeled **8b**, **8c**, (*R*)-**8c** and (*R*)-**8d** were measured. The results are shown in TABLE 1 with the corresponding racemization rate.

TABLE 1 Photoisomerization rates and photoracemization rates of 1,2-di(ethoxycarbonyl)ethyl cobaloxime complexes in the solid-state

	Axial ligand	Rate constants of isomerization s^{-1}	Rate constants of racemization s^{-1}
8b	pyridine	7×10^{-6}	
(*R*)-**4b**	pyridine		2.54×10^{-3}
8c	PMe_2Ph	3×10^{-6}	
(*R*)-**8c**	PMe_2Ph	3.7×10^{-6}	1.03×10^{-2}
(*R*)-**4c**	PMe_2Ph		6.51×10^{-3}
(*R*)-**8d**	(*S*)-1-PEA	2.9×10^{-6}	1.07×10^{-3}
(*R*)-**4d**	(*S*)-1-PEA		1.11×10^{-4}

The results show that the isomerization occurred but the isomerization rates were extremely slow compared with the corresponding racemization rates: for example, the ratios of the racemization rate of 8b with the corresponding isomerization rate was about 350. The fact clearly indicates that contribution of path (c) to the racemization of 1,2-di(alkoxycarbonyl)ethyl complexes was negligibly small. Thus, out-of-plane rotation of radicals and (*E*)-olefins are left as the candidate for the racemization mechanism of (*R*)-2, (*R*)-3, (*R*)-4 and (*S*)-5. When the 180° out-of-plane rotation of (*E*)-olefins occurs, both substituents on C(1) and C(2) make a large movement, and therefore, they are subject to much steric hindrance from the surrounding molecules. In the case of the radicals, however, only the 180° out-of-plane rotation of substituents on C(1) is required (FIGURE 4).

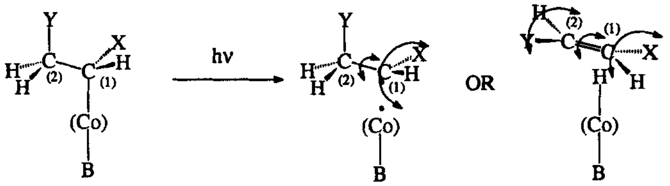


FIGURE 4 180° Out-of-plane rotation of the radical and the (*E*)-olefin

Consequently, the out-of-plane rotation of radicals is to be overwhelmingly easier than that of (*E*)-olefins. Thus, the racemization for (*R*)-2, (*R*)-3, (*R*)-4 and (*S*)-5 is also considered to proceed mainly through path (a), though it probably involves path (b) and/or path (c) to some extent as the minor paths(FIGURE 5).

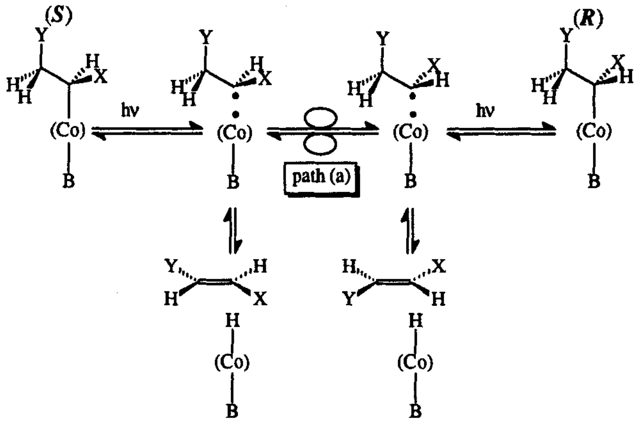


FIGURE 5 Mechanism of solid-state racemization

The above mechanism is supported by rationalization of the interesting and unusual isotope effect that rate constants of D-labeled complexes (*R*)-8c and (*R*)-8d were larger than those of unlabeled complexes (*R*)-4c and (*R*)-4d, respectively (TABLE 1). When out-of-plane rotation of olefin is postulated to be difficult, the racemization rate should mainly depend on the concentration of the radical species. Since the rate of C(2)-H abstraction by Co(II) is much faster than that of the C(2)-D abstraction, the leakage of the radical species of unlabeled complexes to olefins is much larger, in proportion, compared with that of the D-labeled complexes. Thus, the radical concentration in photo-steady state for D-labeled complexes should be much higher than that in the photo-steady state for unlabeled complexes, and in turn, the racemization rates for D-labeled complexes are faster than these for unlabeled complexes.

CONCLUSION

The rate constants of the solid-state photoracemization for the D-labeled chiral 1,2-disubstituted ethyl cobaloxime complexes were larger than those of the isomerization. Futhermore, an interesting and unusual isotope effect was observed: the rate constants of solid-state racemization for D-labeled complexes were larger than those of unlabeled complexes. These results indicate that the solid-state photoracemization proceeds mainly through the 180° out-of-plane rotation of substituents on C(1) atom of radicals .

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