CHEMISTRY LETTERS, pp. 455-458, 1991.

Solid-state Photoracemization of Optically Active Alkyl Cobaloxime Complexes. Solid-state Specific Effect of Axial Ligand

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Solid-state photoracemization of chiral alkyl cobaloxime complexes ocurred with the solid-state specific effect of the axial ligands (the first example of solid state photoracemization). The mechanism is also discussed.

Although X-ray-induced racemizations have been shown to occur in the optically active 1-cyanoethyl cobaloxime complexes,$^{1-5)}$ any solid-state photoracemization has not been reported so far.

In the context of our studies on solid-state reactions of organometallic compounds, we examined photoreactions of optically active 1-cyanoethyl[Y=H,X=CN], 1-(methoxycarbonyl)ethyl[Y=H,X=$COOCH_3$], and 1,2-di(methoxycarbonyl)ethyl[X=Y=$COOCH_3$] cobaloxime complexes coordinated with various axial ligands (Fig. 1) and found that solid-state photoracemization of them occurred and further, an abnormal and solid-state specific effect of axial ligand was observed in the later two series of complexes.

Powdered chiral alkyl cobalt complexes$^{6)}$ suspended in an insoluble liquid such as liquid parafins were irradiated by a solar simulator (Flux density:100 mW/cm^2) at room temperature. In every case TLC of the irradiated sample showed almost single spot. In spite of an aerobic condition alkyl peroxy complexes are not formed, in striking contrast to the solution state reactions which gave alkylperoxy complexes exclusively under an aerobic condition. Optical rotations were measured after purification of the sample by a column chromatography. The optical rotation decreased gradually with irradiated time. The optical rotational change of the initial stage fits first-order rate expression, from which the rate constant was obtained (Table 1).

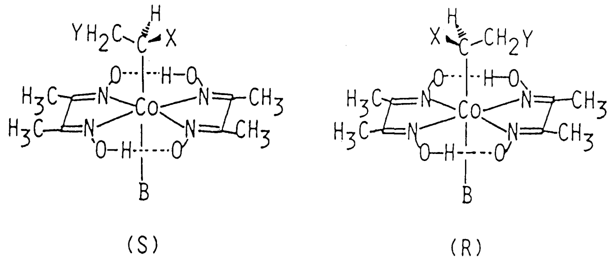


Fig. 1.

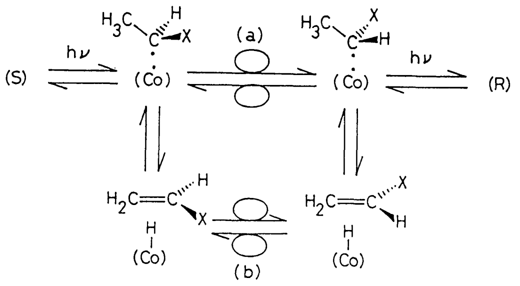
The rate of the photoracemization using bulk crystals is slower by about one order than that of the corresponding powdered sample, but the reaction proceeds without degradation of crystallinity (in cases of (S)-**1i** and (R)-**3h**).

Table 1. Photoracemization Rates of Optically Active 1-Cyanoethyl-, 1-(Methoxycarbonyl)ethyl-, and 1,2-Di(methoxycarbonyl)ethylcobaloxime Complexes in the Solid State

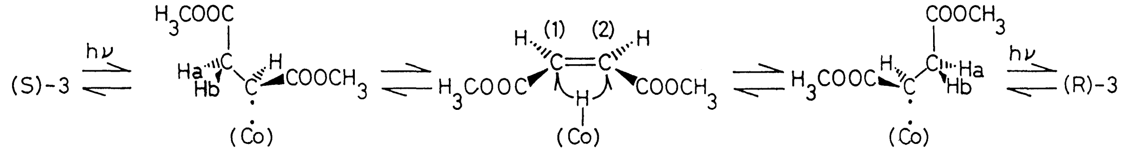
	Substrate			Initial rate constant	Volume of cavity for the reactive group($Å^3$)
	Substituent X	Y	Axial ligand B	s^{-1}	
(R)-**1a**	CN	H	4-CN-pyridine	$1.02x10^{-2}$	(A) 7.97b,c) (B) 10.37
(R)-**1c**	CN	H	pyridine	$1.63x10^{-2}$	(A) 8.89b,d) (B) 11.34
(R)-**1e**	CN	H	(S)-1-PEAa)	$1.46x10^{-2}$	11.53e)
(R)-**1f'**	CN	H	N-Me-imidazole	$0.75x10^{-2}$	7.95f)
(R)-**1g**	CN	H	Bu_3P	$1.16x10^{-2}$	10.64g)
(S)-**1i**	CN	H	Me_2PhP	$2.76x10^{-2}$	17.37f)
(R)-**2a**	$COOCH_3$	H	4-CN-pyridine	$1.58x10^{-4}$	
(S)-**2a**	$COOCH_3$	H	4-CN-pyridine		18.84h)
(R)-**2b**	$COOCH_3$	H	4-Cl-pyridine	$1.03x10^{-3}$	(A) 19.01b,i) (B) 20.22
(R)-**2c**	$COOCH_3$	H	pyridine	$6.49x10^{-3}$	
(R)-**2d**	$COOCH_3$	H	4-Me-pyridine	$6.97x10^{-4}$	
(R)-**2e**	$COOCH_3$	H	(R)-1-PEAa)	$2.30x10^{-6}$	23.83j)
(R)-**2f**	$COOCH_3$	H	imidazole	$3.23x10^{-3}$	
(R)-**2g**	$COOCH_3$	H	Bu_3P	$4.86x10^{-3}$	
(R)-**3c**	$COOCH_3$	$COOCH_3$	pyridine	$1.18x10^{-3}$	(A) 37.55b,k) (B) 45.00
(R)-**3e**	$COOCH_3$	$COOCH_3$	(S)-1-PEAa)	$4.07x10^{-6}$	45.97l)
(R)-**3f'**	$COOCH_3$	$COOCH_3$	N-Me-imidazole	$3.24x10^{-3}$	
(R)-**3h**	$COOCH_3$	$COOCH_3$	$MePh_2P$	$2.54x10^{-2}$	

a) 1-PEA: 1-Phenylethylamine. b) Two crystallographically independent molecules (A) and (B) are involved in the unit cell, and each volume of the cavity is given. c) The volumes of the cavities are for (S)-**1a** (see Ref. 3). d) See Ref. 2. e) See Ref. 1. f) See Ref. 17. g) See Ref. 4. h) See Ref. 12. i) See Ref. 13. j) See Ref. 14. k) See Ref. 15. l) See Ref. 16.

Table 1 shows that the rate of photoracemization of a series of 1-cyanoethyl cobaloximes is remarkably rapid and depends roughly on the volume of the cavity[7]) for the reactive group with little effect of axial ligand, and the difference in rates between the largest and the smallest is not so large. However, the rates of 1-(methoxycarbonyl)ethyl, and 1,2-di(methoxycarbonyl)ethyl complexes are not necessarily dependent on the volume of the cavity for the reactive group, but mainly on the character of the axial base. The rates of the complexes coordinated with 1-phenylethylamine (an alkylamine) were extremely slower (three to four orders of magnitude slower) in each series than those of the complexes coordinated with pyridines, imidazoles, or phosphines. The result is quite different and unexpected from those in the solution-state: in solution there is almost no difference in rates between complexes coordinated with pyridines and that with 1-phenylethylamine.[10]) The reason is not clear at present. Another surprising fact is that the rate of bis(dimethylglyoximato)(methyldiphenylphosphine)[1,2-di(methoxycarboyl)ethyl]cobalt(III), (R)-**3h**, is fastest except for **1i**, though the 1,2-di(methoxycarbonyl)ethyl group is larger and more difficult to move than 1-cyanoethyl and 1-(methoxycarbonyl)ethyl group.



The racemization includes two possible pathways: one is a 180° out-of-plane rotation of the radical formed by photocleavage followed by the recombination [path (a)], and the other proceeds through olefins formed by H-atom abstraction from the initially formed alkyl radical species [path (b)]. Complexes with 1-cyanoethyl (small alkyl) proceed mainly through path (a) and in the cases of 1-(methoxycarbonyl)ethyl and 1,2-di(methoxycarbonyl)ethyl complexes, contribution from path (b) seems to increase: in fact, olefinic protons of methyl acrylate were detected in the ^{1}H-NMR spectrum of irradiated sample of (R)-**2g** while olefinic protons were not detected in the ^{1}H-NMR spectrum of the irradiated sample of 1-cyanoethyl complex under the same condition. In the cases of a series of 1,2-di(methoxycarbonyl)ethyl complexes (**3**), abstraction of Ha or Hb on the alpha-carbon adjacent to the free radical by (Ċo) gives dimethyl fumarate (E-form) or dimethyl maleate (Z-form), respective-



ly. The reaction via (Z)-form olefin, methyl maleate, can afford the racemate by an incidental attack of H-atom to either carbon (1) or (2) without a 180° out-of-plane rotation of the radical. This may explain why **3c**, **3f'** and especially **3h** racemize rather rapidly in spite of having a large alkyl radical.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan (No. 63628007).

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6) Preparation of optically active alkyl cobaloximes **1a-1g**, **2a**, **2c**, **2e**, **3a**, and **3e** was previously reported,$^{8,9,11)}$ and the remainder will be published elswhere.$^{10)}$
7) The cavity for the reactive group is defined as the concave space limited by the envelope surface of the spheres, whose centers are positions of inter- and intramolecular atoms in the neighborhood of the reactive group, the radius of each sphere being greater by 1.2 Å than the van der Waals radius of the corresponding atom (see Refs. 1-4).
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(Received November 13, 1990)