Solid-State Specific and Unidirectional Photoisomerization of 3-Substituted Propyl to 1-Substituted Propyl Cobaloxime Complexes via 2-Substituted Propyl Complexes

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Solid state-specific (γ→β→α)photoisomerization of 3-cyanopropyl and 3-(methoxycarbonyl)propyl cobaloxime complexes were found to occur on visible-light irradiation. There exist considerable differences in the reaction rates, which have no relation to the basicity of the axial ligand. In the former series of complexes, the rate constant (k_2) for the second step (β→α) is much faster than that (k_1) for the first step. However, in the latter series of complexes, the rate constant (k_2) for the second step tends to decrease extremely, and thus, k_2 become smaller than k_1.

Solid-state (solvent free) organic reactions have attracted much attention not only from purely chemical interest but also from the view point of so-called "green chemistry".

We previously reported that 2-substituted ethyl cobaloxime complexes isomerized to 1-substituted ethyl complexes on visible light irradiation in the solid state,[1–3] and the asymmetric (β→α) photoisomerization[2,3] took place when chiral crystals were used. The above mentioned reactions do not occur in solution, and we designate the reactions (that occur only in the solid-state) as "solid-state specific" reactions.

Although solid-state reactions have been rapidly increasing in recent years,[4] reactions which occur only in the solid-state are still extremely rare. It is necessary and important at this stage to accumulate such novel examples and to reveal factors controlling the reaction.

In order to develop a novel and analogous system, we examined whether photoisomerization of 3-substituted propyl cobaloxime complexes could occur in the solid-state, and found the titled reaction which carried quite interesting and unique features. Very recently, Ohashi and his coworkers reported[5] that 4-cyanobutyl(pyridine)cobaloxime complex isomerized to 2-cyanobutyl complex but occurrence of 1-cyanobutyl isomer is not known. The report prompted us to publish our results urgently.

Several 3-cyanopropylcobaloxime complexes (γ-**1a** – γ-**1e**) coordinated with various type of axial ligand [methyldiphenylphosphine (**a**), 3-aminopyridine (**b**), 4-cyanopyridine (**c**), propylamine (**d**), and aniline (**e**)], β- and α-cyanopropyl isomers of γ-**1a** (β-**1a** and α-**1a**) were prepared and characterized by IR and ^{1}H NMR spectra.[6]

A powdered sample of methyldiphenylphosphine-coordinated 3-cyanopropyl cobaloxime complex (γ-**1a**) was suspended in nujol and irradiated with a solar simulator (flux density: 100 mW/cm^2) in the solid state for a set period of time at room temperature, and the sample was analyzed by HPLC using Dicel Chiralcel OD-H (solvent system: hexane/ethanol (93/7)) to obtain the ratio of starting material (γ-substituted complex), 2-cyanopropyl (β-substituted complex), and 1-cyanopropyl (α-substituted complex). The isomerization proceeds rapidly and 93% of the starting material γ-**1a** was converted to isomerized products within 2 hours. The time courses of the ratios of complexes γ-, β-, and α-**1a** are shown in Figure 1 which indicates the reaction to be typically consecutive one. From the first order rate plot of the ratio of the starting material γ-**1a** of the early stage, the rate constant of the first step (γ to β isomerization)($k_1 = 2.0 \times 10^{-3}$ s^{-1}) was obtained. The rate constant of the second step (β to α), k_2, was calculated[7] to be 5.7×10^{-3} s^{-1} by using k_1, initial concentration of γ-complex, and concentration of β-complex at time t in the early stage.

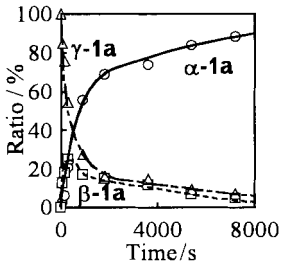


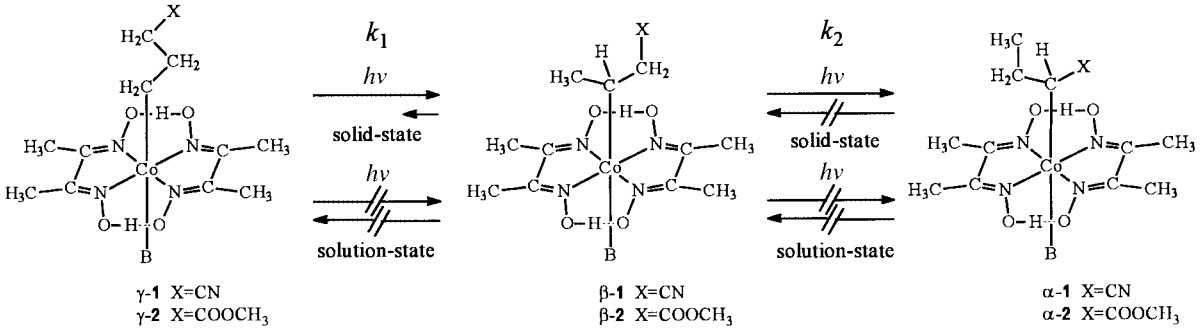
Figure 1. The time courses of complexes, γ-**1a**, β-**1a**, and α-**1a**.

Other 3-cyanopropyl cobaloxime complexes (γ-**1b** – γ-**1e**) were also shown to isomerize similarly. In the cases of these complexes, the axial base was displaced by methyldiphenylphosphine after the reaction, and the resulting sample was analyzed by HPLC to obtain k_1 and k_2 for each reaction. These results are summarized in Table 1 (γ-**1a** – γ-**1e**). The reverse reaction does not occur in the solid-state, and also the (γ→β→α) isomerization does not occur in solution state.

Several 3-(methoxycarbonyl)propyl cobaloxime complexes (γ-**2c**, γ-**2e** and γ-**2n**), and dimethylphenylphosphine-coordinated 2-(methoxycarbonyl)propyl and 1-(methoxycarbonyl)-propyl complexes (β-**2n** and α-**2n**) were also prepared.[8] Photoreactions were carried out as mentioned above. The reaction products were analyzed by HPLC using Dicel OD-H (solvent system: hexane/ethanol (95/5)). From the time courses, rate constants k_1 and k_2 of each reaction were obtained in a similar manner as in the cyanopropyl series. The results are summarized in Table 1 (γ-**2c**, γ-**2e**, and γ-**2n**).

From Table 1, two quite interesting and unique features can be seen: (1) The results show considerable differences in the reaction rates, which have no relation to the basicity of the axial ligand. (2) In the cyano-substituted series of complexes, the reaction rate for the second step (β→α) is much faster than that for the first step (γ→β), on the other hand, in the methoxycarbonyl-substituted series of complexes, the reaction rate for the second step is slower than that for the first step.

Since electronic effect of the axial ligand is shown to be negligible on the rate of the Co–C bond photohomolysis of alkyl cobaloximes in solution state in which intermolecular



Scheme 1.

Table 1. Rate constants, k_1 and k_2, for isomerization of 3-substituted propyl cobaloximes

Substrate			Rate Constants / $10^{-5}s^{-1}$	
Symbol	X	B	k_1	k_2
γ-**1a**	CN	$MePh_2P$	200	570
γ-**1b**	CN	3-Aminopyridine	15	73
γ-**1c**	CN	4-Cyanopyridine	6	33
γ-**1d**	CN	Propylamine	4.5	280
γ-**1e**	CN	Aniline	30	91
γ-**2c**	$COOCH_3$	4-Cyanopyridine	47	5.3
γ-**2e**	$COOCH_3$	Aniline	44	2.7
γ-**2n**	$COOCH_3$	Me_2PhP	27	21

interactions are the same,[9] the rate in the solid-state isomerization should be controlled both by stability of alkyl radical due to capto-dative effect[10] (intramolecular electronic factor) and by intermolecular (lattice-controlled) factor around the reactive group.

Here, the stabilities of the cyano- and methoxycarbonyl-substituted radicals are not so different[11] in solution, so the reaction rates, if compared in each step, will be roughly identical and also k_2 is expected to be greater than k_1 based on the stability of the radicals. Although there are considerable differences in intermolecular interactions (among **1a**–**1e**) both at first step and at second step in the cases of cyanopropyl complexes (as seen from considerable variation both in k_1 and in k_2), k_2 is greater than k_1 in every case when k_1 and k_2 are compared in the reaction of the same substrate. This implies that the difference (in intermolecular interactions) between first and second steps is not so large that k_2 remains to be greater than k_1. On the other hand, in the cases of (methoxycarbonyl)propyl complexes, k_2 became smaller than k_1 in every substrate examined. This seems to imply that intermolecular interaction of the second step become extremely greater than that of the first step.

However, extensive X-ray structural analyses are required for the clear elucidation which will be dealt with in a full paper.

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6 ^{1}H NMR (400 MHz, $CDCl_3$) data for key compounds of cyanopropyl series γ-**1a**; δ 7.37 (m, 10H, aromatic), 2.19 (t, 2H, *J* 8.9 Hz, $–CH_2–CN$), 1.84 (d, 3H, $J_{H–P}$ = 8.1 Hz, $P–CH_3$), 1.80 (d, 12H, $J_{H–P}$ = 3.4 Hz, CH_3 of dmgH(dmgH: dimethylglyoximato mono anion)), 1.64 (m, 2H, $Co–CH_2–$), 1.28 (m, 2H, $CoCH_2–CH_2–$), β-**1a**; δ 7.38 (m, 10H, aromatic), 2.38 (ddd, 1H, *J* = 4.4 Hz, *J* = 7.1 Hz, and *J* = 17.1 Hz, –CHH–CN), 2.04 (ddd, 1H, *J* = 2.9 Hz, *J* = 9.0 Hz, and *J* = 17.1 Hz, –CHH–CN), 1.84 (d, 3H, $J_{H–P}$ = 8.1 Hz, $P–CH_3$), 1.81 (d, 6H, $J_{H–P}$ = 3.7 Hz, CH_3 of dmgH), 1.80 (d, 6H, $J_{H–P}$ = 3.7 Hz, CH_3 of dmgH), 1.40 (m, 1H, Co–CH–), 0.77 (dd, 3H, $J_{H–P}$ = 7.3 Hz and *J* = 7.3 Hz, $CoCH–CH_3$), and α-**1a**; δ 7.43 (m, 10H, aromatic), 2.20 (m, 1H, Co–CH–), 1.89 (d, 3H, $J_{H–P}$ = 9.3 Hz, $P–CH_3$), 1.88 (d, 6H, $J_{H–P}$ = 3.2 Hz, CH_3 of dmgH), 1.84 (d, 6H, $J_{H–P}$ = 3.2 Hz, CH_3 of dmgH), 1.10 (m, 1H, $CoCH–CHH–CH_3$), 0.97 (t, 3H, *J* = 7.0Hz, $CoCHCH_2–CH_3$), 0.89 (m, 1H, CoCH–CHH–CH_3).
7 k_2 was calculated by applying the rate expression for consecutive reaction, $[\beta\text{-}\mathbf{1}]_t = [\gamma\text{-}\mathbf{1}]_0\, k_1(e^{-k_1 t} - e^{-k_2 t})/(k_2 - k_1)$where $[\beta\text{-}\mathbf{1}]_t$, $[\gamma\text{-}\mathbf{1}]_0$, k_1, and k_2 are concentration of β-**1** at time t, initial concentration of γ-**1**, rate constant of the first step, and that of the second step, respectively.
8 ^{1}H NMR (400 MHz, $CDCl_3$) data for key compounds of (methoxycarbonyl)propyl series γ-**2n**; δ 7.35 (m, 3H, aromatic), 7.10 (m, 2H, aromatic), 3.57 (s, 3H, $–OCH_3$), 2.18 (t, 2H, *J* = 7.4 Hz, $–CH_2–COOCH_3$), 1.93 (d, 12H, $J_{H–P}$ = 3.4 Hz, CH_3 of dmgH), 1.58 (m, 2H, $Co–CH_2–$), 1.39 (d, 6H, $J_{H–P}$ = 9.0 Hz, $P–(CH_3)_2$), 1.25 (m, 2H, $CoCH_2–CH_2–$), β-**2n**; δ 7.34 (m, 3H, aromatic), 7.09 (m, 2H, aromatic), 3.56 (s, 3H, $–OCH_3$), 2.63 (m, 1H, CoCH–CHH–), 1.94 (d, 12H, $J_{H–P}$ = 3.6 Hz, CH_3 of dmgH), 1.64 (m, 2H, Co–CH–CHH–), 1.37 (d, 6H, $J_{H–P}$ = 9.3 Hz, $P–(CH_3)_2$), 0.61 (dd, 3H, $J_{H–P}$ = 6.6 Hz and *J* = 6.6 Hz, $CoCH–CH_3$), and α-**2n**; δ 7.36 (m, 3H, aromatic), 7.11 (m, 2H, aromatic), 3.44 (s, 3H, $–OCH_3$), 1.99 (d, 6H, $J_{H–P}$ = 3.2 Hz, CH_3 of dmgH), 1.97 (d, 6H, $J_{H–P}$ = 3.2 Hz, CH_3 of dmgH), 1.87 (m, 1H, Co–CH–), 1.38 (d, 3H, $J_{H–P}$ = 10.0 Hz, $P–CH_3$), 1.37 (d, 3H, $J_{H–P}$ = 10.0 Hz, $P–CH_3$), 1.20 (m, 2H, $CoCH–CH_2–$), 0.73 (t, 3H, *J* = 7.2 Hz, $CoCHCH_2–CH_3$).
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