Alkyl Radical Substitution on Disulfide in the Presence of Cobalt(II) Complexes

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Photolysis of methyl(L)cobaloxime (L=trans ligand) (**1**) or methyl(L)-*O*,*O*′-bis(difluoroboryl)cobaloxime (**2**) in the presence of bis(4-chlorophenyl) disulfide gave 4-chlorophenyl methyl sulfide together with 4-chlorophenylthio(L)cobaloxime (**5**) or 4-chlorophenylthio(L)-*O*,*O*′-bis(difluoroboryl)cobaloxime (**6**). Similar photolysis in the presence of 2,2,6,6-tetramethyl-1-piperidyloxyl (TEMPO) gives 1-methoxy-2,2,6,6-tetramethylpiperidine. The reactivity of the cobaloximes **1** and **2** to the disulfide and TEMPO increases when the cobaloximes have a trans ligand (L) of larger steric requirement and low *pka*, or when the equatorial ligand is an electronegative *O*-(difluoroboryl)dimethylglyoxime. Two probable mechanisms are proposed for the reaction. The first is a direct radical substitution on the disulfide with a methyl radical, and the second involves the initial interaction between the disulfide and the (L)cobaloxime radical to afford arylthio(L)cobaloxime (**5** or **6**) and an arylthio radical. The latter radical reacts with methyl(L)cobaloxime to give aryl methyl sulfide.

Among biological C_1-transfer, S-methylation by ^{5}N-methyltetrahydrofolate[1] is of central importance in relation to the biosyntheses of methionine[2] and methylcoenzyme M.[3] These S-methylations are mediated by cobalt–corrin complexes.[2,3] Mechanistic studies on radical substitution on sulfur have attracted current interest of theoreticians[4] and experimentalists.[4a,5] We have been studying the substitution on sulfur by alkyl radicals in the presence of a cobalt complex,[6] which may simulate an enzymic methyl transfer from cobalt to sulfur. The reaction is considered to proceed through a λ^4-sulfanyl radical as an intermediate or a transition state.[6]

Radical substitution on disulfide has been known for over two decades.[7] Recent studies have dealt with the substitution by the radicals generated from cobalt complexes,[8] but no study has clarified the relation between the structure of the cobalt complex and the reactivity.

Herein we describe the electronic and steric effect of the ligand of cobalt complexes on the radical substitution on disulfide, an alkyl transfer from cobalt to sulfur. A higher level of the HOMO of disulfide[9] may define its role in such a substitution reaction since the strong interaction between the HOMO of disulfide and cobalt(II) can be expected.

Bis(dimethylglyoximato)(L)methylcobalt(III)[10] (L denotes a trans ligand) (**1**) (Fig. 1), hereafter methyl(L)cobaloxime or CH_3(L)[Co], was photolyzed in the presence of bis(4-chlorophenyl) disulfide (**3**) by 350 nm region lamps in benzene or acetonitrile. Only 4-chlorophenyl methyl sulfide (**4**) was isolated as an organic product (Scheme 1) and the control experiment without irradiation gave no sulfide **4**. Benzene or acetonitrile was chosen for experimental convenience, and no solvent effect was seen.

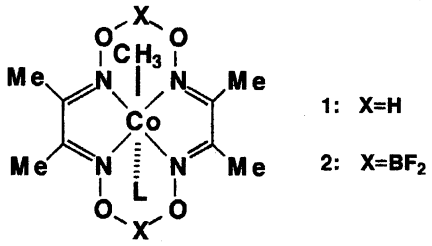
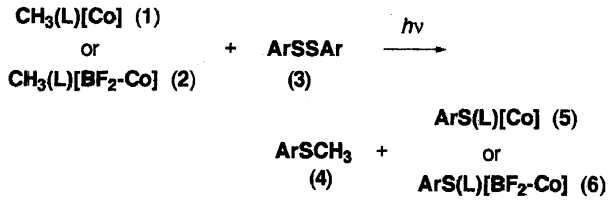


Fig. 1. Methyl(L)cobaloxime (**1**) and Methyl(L)BF_2-cobaloxime (**2**).

All the photoreactions were done under identical conditions using a merry-go-round type photoreactor (see Experimental section) and the reactions were stopped at an early stage or before completion to get information about the relative reactivity. The course of the reaction was not traced because of opacity of the solu-



Scheme 1.

tion at later stages. The trans phosphine ligands of **1** exchange slowly with the disulfide in the reaction system. The exchange, however, was less than 10% with the cobaloximes under these reaction conditions and the order of the reactivity of the cobaloximes was not affected by the ligand exchange. Photolysis of disulfides has been reported to take place with a short-wavelength UV light.[11] A Pyrex® filtered light, however, splits the disulfide inefficiently, if at all, and the generation of the arylthio radical from this process is neglected in the following discussions.

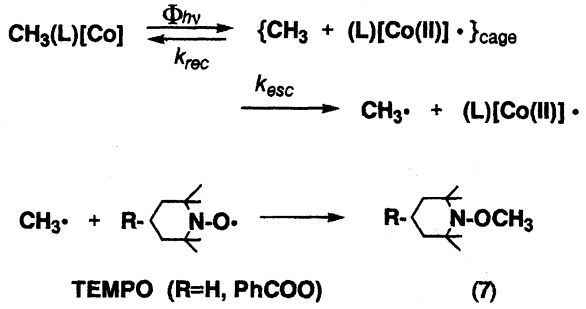
Due to these experimental limitations, the yields of sulfide **4** do not give the relative rate of the reaction but indicate the reactivity order, and the discussions must be qualitative. The results were reproducible and the order of reactivities can be reasonably estimated from the relative yields of sulfide **4** under these conditions.

As seen in Table 1, the yield of sulfide **4** varies by the nature of phosphines used as a trans ligand (L). The rate and efficiency of the homolysis of a cobalt–alkyl bond have been reported to depend on the steric bulkiness (cone angle) of phosphine.[12,13] This radical substitution also shows the relationship with the cone angle and *pka*'s of the trans phosphine ligand.[12—14] A similar trend is seen in the reaction of methyl(L)cobaloxime (**1**) having a 4-substituted pyridine as a trans ligand (L) (Table 1). The yield of sulfide **4** increases by changing the ligand to a less basic pyridine derivative.[15] The ligand effect is more evident when the planar ligand, dimethylglyoxime, in cobaloxime **1** is replaced by *O*-(difluoroboryl) dimethylglyoxime. Methyl(L)-bis(*O*,*O*'-difluoroboryl)cobaloxime (**2**) (Fig. 1) reacts faster than the corresponding methyl(L)cobaloxime (**1**) under the identical conditions. A BF_2 group is more electronegative than hydrogen[16] as evidenced by the rise of reduction potentials[17] and the decrease of nucleophilicity[18] of BF_2-cobaloxime **2**. The central cobalt, therefore, becomes more electronegative in BF_2-cobaloxime **2**.

The probable origin of those ligand effects on the reaction is the effective concentration of the methyl radical and the penta-coordinated (L)cobaloxime(II) under the photolytic conditions. Another important factor is the affinity of the (L)cobaloxime(II) for sulfur.

The concentrations of the photolysis solutions were adjusted to completely absorb the light of the 350 nm region. Therefore, the effective concentrations of the out-of-cage methyl and (L)cobaloxime radical must be governed by the quantum yield of the cobalt–methyl bond homolysis ($\phi_{h\nu}$), the in-cage recombination rate of the radical pair (k_{rec}), and the rate of escape from the solvent cage (k_{esc}) (Scheme 2).

Finke et al.[19] reported that the out-of-cage methyl radical can be trapped by 2,2,6,6-tetramethyl-1-piperidyloxyl (TEMPO) with a diffusion-controlled rate. We confirmed that TEMPO of 10^{-3}—10^{-2} mol dm^{-3} gave the constant yields of 1-methoxy-2,2,6,6-tetramethylpiperidine (methyl-TEMPO) (**7**), and hence the out-of-cage methyl radical from methyl(L)-



Scheme 2.

Table 1. Photolyses of Methyl(L)cobaloximes (**1**) and Methyl(L)BF_2-cobaloximes (**2**) in the Presence of Bis(4-chlorophenyl) Disulfide (**3**)[a,b] or TEMPO[c,d]

Cobaloxime	L	4	7	Cone	*pka* of L[14,15]
		Yield/%	Yield/%	angle[12,13]	
1a	PPh_3	25	67	159	2.7
1b	PPh_2Bu	13	39	140	5.0
1c	PBu_3	7	28	129	8.4
1d	4-CN-Py	40	29	—	1.9
1e	Py	32	28	—	5.2
1f	4-^{t}Bu-Py	28	25	—	5.9
2a	4-CN-Py	67	67	—	1.9
2b	Py	62	65	—	5.2
2c	4-^{t}Bu-Py	59	57	—	5.9

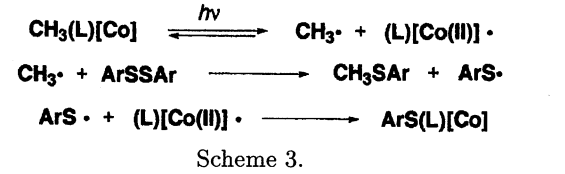
a) CH_3(L)cobaloxime (**1a**—**1c**) (3.0×10^{-3} mol dm^{-3}) and [(4-ClC_6H_4)S]$_2$ (2.0×10^{-2} mol dm^{-3}) in benzene. Irradiation: 1.2 h. b) CH_3(L)cobaloxime (**1d**—**1f**) or CH_3(L)BF_2-cobaloxime (**2a**—**2c**) (3.0×10^{-3} mol dm^{-3}) and [(4-ClC_6H_4)S]$_2$ (2.0×10^{-2} mol dm^{-3}) in acetonitrile. Irradiation: 10 h. c) CH_3(L)-cobaloxime (**1a**—**1f**) (6.0×10^{-3} mol dm^{-3}) and TEMPO (9.0×10^{-2} mol dm^{-3}) in benzene. Irradiation: 1/2 h. d) CH_3(L)BF_2-cobaloxime (**2a**—**2c**) (6.0×10^{-3} mol dm^{-3}) and 4-benzoyloxy-TEMPO (1.3×10^{-2} mol dm^{-3}) in acetonitrile. Irradiation: 1/2 h.

cobaloximes can be completely trapped (Scheme 2). The effective concentration of the out-of-cage methyl radical from the cobaloximes, therefore, can be estimated by the yields of methyl-TEMPO **7**. Results from the photolyses of methyl(L)cobaloximes and methyl(L)-BF_2-cobaloximes (**1** and **2**) in the presence of TEMPO ($1.3—9.0\times10^{-2}$ mol dm^{-3}) are shown in Table 1.

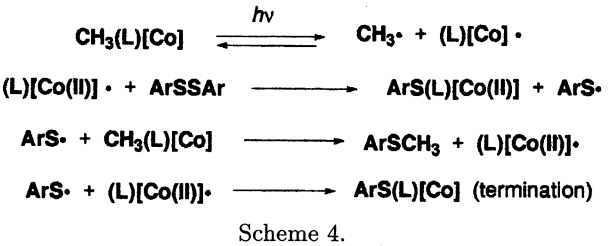
As seen in Table 1, the yields of methyl-TEMPO **7** rely on both the cone angle and the basicity of phosphine ligand. 4-Substituted pyridines have essentially the same steric shielding and the yields of **7** are modestly affected by the basicity of pyridine derivatives. These results are in good accordance with the effect of trans ligands to the cobalt–alkyl bond energy.[20] Methyl radical reacts with a disulfide to give a methyl sulfide (Scheme 3).[7,8] These discussions support the mechanism of this radical substitution as depicted in Scheme 3.

Irradiation of methyl(pyridine)cobaloxime (**1e**) at −196 °C in CD_3OH gave ESR signals of methyl and (pyridine)cobaloxime radicals.[21] The same cobaloximes was irradiated in the presence of a sulfide at −80 °C to annihilate the methyl radical and the ESR measurement at −130 °C gave the signal of the (pyridine)cobaloxime radical coordinated with the sulfide as a sixth ligand.[22] Similar irradiation of cobaloxime **1e** in the presence of dimethyl disulfide, however, did not show the survival of the (pyridine)cobaloxime radical. These findings suggest a fast reaction between the (L)cobaloxime radical, (L)[Co(II)], and the disulfide even at −80 °C to give arylthio(L)cobaloxime and the arylthio radical (Scheme 4). In fact this is a practical preparation process for arylthio(pyridine)cobaloxime.[23] From the discussions above, an alternative mechanism of the present radical substitution is shown in Scheme 4.

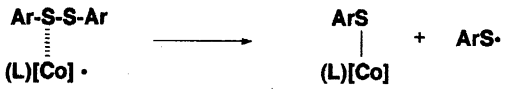
An alkylthio radical has been reported to react efficiently with alkyl(L)cobaloxime[24] to give a sulfide and an (L)cobaloxime radical (Scheme 4). The radical substitution on disulfide by the (L)cobaloxime radical and the reaction of the arylthio radical with methyl(L)cobaloxime can be a chain reaction, but the termination to give arylthio(L)cobaloxime should be efficient (Scheme 4).



Scheme 3.



Scheme 4.



Scheme 5.

These two processes (Schemes 3 and 4) to afford aryl methyl sulfide are considered to depend on the effective concentrations of the out-of-cage methyl radical (Scheme 3) and the concentration of arylthio radical (Scheme 4). We cannot measure the relative importance of the two mechanisms for the production of aryl methyl sulfide. Our ESR study,[22] however, suggests a fast reaction between (L)cobaloxime radical and disulfide to give arylthio radical efficiently, and the role of (L)cobaloxime complex in these reactions is envisaged. The coordination of sulfide to the cobalt(II) complex is effective and the cobalt–sulfur complex is an observable entity with sulfide.[22] The interaction with disulfide, on the other hand, may be as strong as expected from its raised HOMO level. This strong interaction together with the weakness of the disulfide bond drives the hypothetical cobalt–disulfide complex into arylthio(L)cobaloxime and an arylthio radical (Scheme 5).

Experimental

Syntheses of Methyl(L)cobaloximes. Methyl(L)cobaloximes, **1a** (L=PPh_3),[25] **1e** (L=Py),[11] and **1f** (L=4-^{t}Bu-Py)[26] were prepared directly from $CoCl_2\cdot6H_2O$, and the ligands under reduction conditions.[10] Methyl(L)cobaloximes, **1b** (L=PPh_2Bu), **1c** (L=PBu_3),[25] and **1d** (L=4-CN-Py)[27] were prepared by the ligand exchange of methyl(H_2O)cobaloxime[25] in refluxing benzene. All known cobaloximes (**1a**, **1c**, **1d**, **1e**, and **1f**) gave satisfactory elemental analyses and spectral date.

Cobaloxime **1b**, mp 151 °C (decomp); ^{1}H NMR (90 MHz, $CDCl_3$) δ=0.80 (3H, t, J_p=6.0 Hz), 0.90—2.60 (6H, m), 1.06 (3H, d, J_p=4.0 Hz), 1.82 (12H, d, J_p=3.4 Hz), 7.02—7.35 (10H, m), 18.08 (2H, br s). Found: C, 54.99; H, 6.74; N, 10.20%. Calcd for $C_{25}H_{36}N_4O_4PCo$: C, 54.95; H, 6.64; N, 10.25%.

Syntheses of Methyl(L)BF_2-cobaloximes. (4-Cyanopyridine)methylbis(difluoroboryl)cobaloxime (**2a**) was prepared by the ligand exchange of methyl(H_2O)BF_2-cobaloxime[25] with 4-cyanopyridine in dichloromethane at ambient temperature. Methyl(L)BF_2-cobaloxime **2b** (L=Py)[25] and **2c** (L=4-^{t}Bu-Py) were prepared by treating cobaloxime **1e** and **1f** (1.6 mmol), respectively, with BF_3-etherate (8.1 mmol) in 1.0 cm^3 of dichloromethane at ambient temperature, and recrystallized from dichloromethane–ether using diffuse mixing of the solvents.

Cobaloxime **2a**, mp 218.0—218.5 °C (decomp); ^{1}H NMR (90 MHz, $CDCl_3$) δ=1.41 (3H, s), 2.35 (12H, s), 7.62 (2H, dd, J=4.9 and 1.3 Hz), 8.20 (2H, dd, J=4.9 and 1.4 Hz). Found: C, 35.75; H, 3.80; N, 16.68%. Calcd for $C_{15}H_{19}B_2F_4N_6O_4Co$: C, 35.71; H, 3.73; N, 16.76%.

Cobaloxime **2c**, mp 212.0—213.0 °C (decomp); ^{1}H NMR (90 MHz, CD_2Cl_2) 1.29 (9H, s), 1.40 (3H, s), 2.35 (12H, s), 7.3 (2H, dd, J=5.9 and 1.6 Hz), 8.01 (2H, dd, J=5.9 and

1.6 Hz). Found: C, 40.13; H, 5.15; N, 13.09%. Calcd for $C_{18}H_{28}B_2F_4N_5O_4Co$: C, 40.41; H, 5.28; N, 13.09%.

Photochemical Reaction of Methyl(L)cobaloximes (1a—1f) and Methyl(L)BF_2-cobaloximes (2a—2c) with Bis(4-chlorophenyl) Disulfide (3). To the disulfide **3** (20 mmol dm^{-3}) in 14 cm^3 of benzene or acetonitrile was added one of the cobaloximes (**1a**—**1f** and **2a**—**2c**, 3.0 mmol dm^{-3}). The solutions containing different cobaloximes were placed in tube type reaction vessels (14.5 mm diameter) of Pyrex® and degassed by bubbling argon through syringe needles under ultrasonic irradiation. The degassed solutions were irradiated under identical conditions with a merry-go-round type photoreactor (Rayonett RPR-100) equipped with lamps (RPR-3500A) that radiate 350 nm light. The reaction mixtures were concentrated, and the persisting cobaloximes (**1** or **2**) and the arylthio(L)cobaloxime (**5** or **6**) as well as polar degradation products were removed by chromatography on silica gel with the use of hexane–dichloromethane (65 : 35) as a developing solvent. The eluent containing the starting disulfide **3** and the product sulfide **4** were adjusted to the same volume and analyzed by gas chromatography on a semicapillary column coated with SE-30 (N_2). The analyses showed only one organic product beside the starting disulfide **3**. The product was identified with 4-chlorophenyl methyl sulfide (**4**) by comparison of the mass spectra of the authentic sample. Yields of the sulfide **4** were measured by the gas chromatography using 1, 3-dimethoxybenzene as an internal reference. The reaction conditions are recorded as footnotes of Table 1. 4-Chlorophenylthio(L)cobaloximes were separated from the product mixtures by chromatography on Florisil® eluted with chloroform and identified with the authentic sample.

Photochemical Reaction of Methyl(L)cobaloximes (1a—1f) and Methyl(pyridine)BF_2-cobaloximes (2a—2c) with TEMPOs. The mixture of the cobaloximes and TEMPO was irradiated in the same manner as recorded for the photoreaction of the cobaloximes with the disulfide. The reaction conditions are recorded as footnotes of Table 1. The products, methyl-TEMPO (**9a**)[28] or 4-benzoyloxy-1-methoxy-2,2,6,6,-tetramethylpyperidine (**9b**)[29] were identified with authentic samples and determined by gas chromatography by the same procedure recorded for the photoreaction with the disulfide.

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