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Reactions of the Octahedral Bis(α-diketone dioximato)iron(II) Complexes with Carbon Monoxide and Benzyl Isocyanide

Yoshihiro Sasaki
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

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The reactions of bis(α-diketone dioximato)iron(II) coordinated by two nitrogeneous base molecules (X) with carbon monoxide and benzyl isocyanide were studied kinetically in chloroform; here α-diketone dioxime= 2,2′-difurylglyoxime (H_2fr) and dimethylglyoxime (H_2dg). The reactions proceeded reversibly through a dissociative mechanism. For the reaction $\mathrm{Fe(Hfr)_2(X)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(Hfr)_2(X)} + \mathrm{X}$, plots of log k_1 *vs.* pK_a (K_a: dissociation constant of conjugate acid of base) for pyridines gave a negative correlation. The log k_1 values of 4-cyanopyridine and 4-acetylpyridine systems were smaller and that of 2,6-dimethylpyridine system larger than predicted by their pK_a values. Imidazole and 1-methylimidazole were more inert than pyridines. For the reaction $\mathrm{Fe(Hfr)_2(X)} + \mathrm{CO} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Fe(Hfr)_2(X)(CO)}$, log k_{-2} *vs.* pK_a plots for sterically unhindered pyridines showed a linear relationship, but the basicity of pyridine bases did not affect the CO dissociation processes very much. 2-Methylpyridine, 2,4-dimethylpyridine, and 2,6-dimethylpyridine facilitated the dissociation of CO slightly as compared with pyridine. Imidazole and 1-methylimidazole allowed CO to be more inert and piperidine more labile than pyridines. The dissociation of the base was significantly affected by the change of substituents in α-diketone dioxime, and the dissociation of CO was slightly affected by the change of substituents. The reaction behavior was discussed on the basis of the activation parameters and infrared data.

Many investigations have been reported on axial ligand substitution reactions in six-coordinated iron(II) complexes containing macrocyclic ligands.1—12) In such complexes the equatorial positions are occupied by four nitrogen atoms of the macrocycles and the axial sites by the ligands taking part in the observed rate processes. All the complexes investigated so far are able to bind carbon monoxide reversibly at the sixth position. The reactions proceed through a dissociative mechanism involving a five-coordinated intermediate which is very reactive. The binding processes of five-coordinated iron(II) porphyrins with bases and CO, which are related to biological functions of hemoproteins, have been studied using flash- or laser-photolysis techniques.13—16) On the other hand, studies of axial ligand substitution reactions for six-coordinated iron(II) complexes with macrocycles may offer useful information on the dissociative processes of axial ligands such as nitrogeneous bases, CO, and O_2 in iron(II) porphyrins.

Octahedral bis(α-diketone dioximato)iron(II) containing a nitrogeneous base possesses a similar structure to that of iron(II) porphyrins and is able to bind CO reversibly.17,18) Vaska and Yamaji have studied reactions of bis(diphenylglyoximato)iron(II) with CO; they proposed that the reactions proceed *via* a five-coordinated intermediate.19) Pang and Stynes have reported the rate parameters for dissociation of base, CO, and benzyl isocyanide in bis(dimethylglyoximato)-iron(II) systems at low and high temperatures.20) In the reaction systems studied so far, pyridine, 1-methylimidazole, and piperidine have been used as bases.2,3,5,20) The factors regulating such reactions are not sufficiently understood. The reactivity of iron atom in these complexes is thought to be affected by the properties of the axial ligand as well as by the properties of the equatorial macrocycle. In this study, the reactions of bis(2,2′-difurylglyoximato)iron(II), $\mathrm{Fe(Hfr)_2(X)_2}$ (X=base), with CO and benzyl isocyanide have been investigated in order to reveal the basicity effect and the steric effect of axial ligands on the reactions, and the reactions of bis(dimethylglyoximato)iron(II), $\mathrm{Fe(Hdg)_2(X)_2}$ (X=pyridine and 1-methylimidazole), with CO have been re-examined in order to compare them with $\mathrm{Fe(Hfr)_2(X)_2}$–CO systems.

Experimental

Materials. Pyridine (py), 2-methylpyridine (2-mepy), 4-methylpyridine (4-mepy), 2,6-dimethylpyridine (2,6-$\mathrm{me_2py}$), 2,4-dimethylpyridine (2,4-$\mathrm{me_2py}$), 3,4-dimethylpyridine (3,4-$\mathrm{me_2py}$), 4-acetylpyridine (acpy), 3-chloropyridine (3-clpy), 1-methylimidazole (meim), butylamine (buam), and piperidine (pip) were distilled from KOH solutions prior to use. 4-Cyanopyridine (cnpy) and 4-dimethylaminopyridine (dmnpy) were purified by recrystallization. 2,2′-Difurylglyoxime (H_2fr), dimethylglyoxime (H_2dg), and imidazole (im) of guaranteed grade were used without further purification. 4-Chloropyridine (4-clpy) was prepared from 4-chloropyridine hydrochloride according to Lavalette *et al.*16) Solutions of 4-clpy in chloroform were stored in a refrigerator. Guaranteed grade chloroform was used as solvent and carbon monoxide was obtained commercially. Benzyl isocyanide (bzlnc) was prepared according to the procedure described by Ugi and Meyer.21)

Preparation of Complexes. Iron(II) dimethylglyoxime complexes, $\mathrm{Fe(Hdg)_2(X)_2}$ (X=py and meim), and some iron(II) 2,2′-difurylglyoxime complexes, $\mathrm{Fe(Hfr)_2(X)_2}$ (X= py, meim, 4-mepy, and cnpy), were prepared according to the methods reported previously.22) $\mathrm{Fe(Hdg)_2(X)(CO)}$ and $\mathrm{Fe(Hdg)_2(X)(bzlnc)}$ (X=py and meim) were prepared according to the procedures described by Pang and Stynes.20)

$\mathrm{Fe(Hfr)_2(3\text{-}clpy)_2}$: Methanol–water solutions of Mohr's salt (0.4 g) and 2,2′-difurylglyoxime (0.4 g) were mixed together under a nitrogen atmosphere and then 3-chloropyridine (2 ml) was added to the mixture. The pH value of the mixed solution was adjusted to about 7 by adding an aqueous NaOH solution to precipitate reddish brown crystals.

Table 1. Analytical data of new complexes

Compound	Found(Calcd)(%)			
	C	H	N	Cl
Fe(Hfr)$_2$(3-clpy)$_2$	49.42	2.98	11.66	
	(49.95)	(3.08)	(11.65)	
Fe(Hfr)$_2$(acpy)$_2$	54.77	4.37	11.35	
	(55.45)	(3.83)	(11.41)	
Fe(Hfr)$_2$(3,4-me$_2$py)$_2$	57.24	4.21	11.90	
	(57.63)	(4.55)	(11.86)	
Fe(Hfr)$_2$(dmnpy)$_2$	53.92	4.55	14.63	
	(55.29)	(4.64)	(15.18)	
Fe(Hfr)$_2$(im)$_2$H$_2$O	47.59	3.34	17.12	
	(48.16)	(3.73)	(17.19)	
Fe(Hfr)$_2$(py)(CO)	51.92	3.22	11.45	
	(51.93)	(3.19)	(11.65)	
Fe(Hfr)$_2$(meim)(CO)	49.07	3.43	14.30	
	(49.68)	(3.34)	(13.91)	
Fe(Hfr)$_2$(3-clpy)(CO)	49.31	3.44	9.62	
	(49.12)	(2.85)	(11.02)	
Fe(Hfr)$_2$(py)(bzlnc)-CH$_2$Cl$_2$	52.32	3.56	11.24	9.44
	(52.66)	(3.64)	(10.84)	(9.14)
Fe(Hfr)$_2$(meim)(bzlnc)	55.21	3.90	14.22	
	(55.42)	(3.93)	(14.14)	
Fe(Hfr)$_2$(3-clpy)(bzlnc)	54.31	3.49	11.36	3.50
	(54.67)	(3.48)	(11.60)	(4.89)
Fe(Hfr)$_2$(buam)(bzlnc)	55.42	4.47	11.94	
	(56.15)	(4.71)	(12.28)	

Fe(Hfr)$_2$(py)(CO): A solution of Fe(Hfr)$_2$(py)$_2$H$_2$O (700 mg) in dichloromethane (200 ml) was stirred for 12 h under a CO atmosphere in the dark and concentrated to about 25 ml by bubbling CO. The brown crystals were precipitated by the addition of petroleum ether (70 ml) to the concentrated solution.

Fe(Hfr)$_2$(py)(bzlnc)CH$_2$Cl$_2$: Fe(Hfr)$_2$(py)$_2$H$_2$O (500 mg) was added to 50 ml of dichloromethane containing benzyl isocyanide (350 mg) and pyridine ($\approx 10^{-3}$ mol dm^{-3}). The solution was stirred for 6 h and concentrated to about 20 ml by bubbling N$_2$. Petroleum ether (70 ml) was added to the solution to precipitate the black crystals.

Fe(Hfr)$_2$(acpy)$_2$, Fe(Hfr)$_2$(3,4-me$_2$py)$_2$, Fe(Hfr)$_2$(dmnpy)$_2$, Fe(Hfr)$_2$(im)$_2$, Fe(Hfr)$_2$(meim)(CO), Fe(Hfr)$_2$(3-clpy)(CO), Fe(Hfr)$_2$(meim)(bzlnc), Fe(Hfr)$_2$(3-clpy)(bzlnc), and Fe(Hfr)$_2$(buam)(bzlnc) were prepared by the procedures described above. The analytical results of these new complexes are shown in Table 1.

Physical Measurements. Visible spectra were obtained on a Hitachi 323 automatic recording spectrophotometer, equipped with a thermostated cell-holder and connected with a vacuum line. Infrared spectra were measured in Nujol mull or KBr disk with a Perkin-Elmer 521 spectrophotometer.

Fe(Hfr)$_2$(X)$_2$, Fe(Hdg)$_2$(X)$_2$, and Carbonyl Complex Samples. Solutions of Fe(Hfr)$_2$(X)$_2$ (X=py, 4-mepy, cnpy, 3-clpy, acpy, dmnpy, 3,4-me$_2$py, im, and meim) ($\approx 3\times10^{-4}$ mol dm^{-3}) and Fe(Hdg)$_2$(X)$_2$ (X=py and meim) ($\approx 6\times10^{-4}$ mol dm^{-3}) were prepared by dissolving isolated complexes in chloroform containing a large excess of the bases to prevent oxidation of the complexes. Solutions of the other 2,2′-difurylglyoxime complexes (X=buam, 2-mepy, 2,4-me$_2$py, 2,6-me$_2$py, 4-clpy, and pip) ($\approx 3\times10^{-4}$ mol dm^{-3}) were prepared by dissolving Fe(Hfr)$_2$(3-clpy)$_2$ or Fe(Hfr)$_2$(py)$_2$ in chloroform containing the bases. Carbonyl complexes were prepared by bubbling CO through bis(base) complex solutions for 2—4 h.

Kinetics. For the reactions of Fe(α-diketone dioximato)$_2$(X)$_2$ with CO or bzlnc, a 0.3 ml portion of a bis(base) complex solution was syringed into a serum-capped chloroform solution (2.7 ml) over 1 atm. CO or 10^{-3}—5×10^{-3} mol dm^{-3} bzlnc. The substitution reaction of Fe(α-diketone dioximato)$_2$(X)(CO) with base (X) was carried out by syringing 0.3 ml of a carbonyl complex solution bubbled with N$_2$ for 2 min into chloroform containing a large excess of base ([X]$>10^{-1}$ mol dm^{-3}) or into base (2.7 ml). The kinetic measurement was made by monitering the absorbance change at a constant temperature (±0.2 °C). The experimental conditions, where the axial ligands were kept in large excess against the complexes ($\approx 3\times10^{-5}$ mol dm^{-3}), gave rise to pseudo-first-order rate constants. The rate constant, k_{obsd}, was evaluated from the $\ln(A-A_\infty)$ *vs.* time plots, which were linear or at least 3-half-lives.

Results and Discussion

Fe(Hfr)$_2$(X)$_2$ (X=py, 4-mepy, 3-clpy, cnpy, acpy, 3,4-me$_2$py, dmnpy, im, and meim) and Fe(Hdg)$_2$(X)$_2$ (X=py and meim) were synthesized in methanol–water (1:1 volume ratio) containing a large excess of the bases. The complexes were oxidized readily in chloroform, but the oxidation was suppressed by the presence of the bases. The H$_2$fr complexes were more stable than the H$_2$dg complexes. The other H$_2$fr complexes (X=pip, 2-mepy, 2,4-me$_2$py, and 2,6-me$_2$py) were oxidized immediately in methanol–water containing a large excess of the bases, but the complexes in chloroform were fairly stable in the presence of the bases. The carbonyl and bzlnc complexes in solution displayed photodissociation of CO and bzlnc, respectively. The preparation of Fe(Hfr)$_2$(cnpy)(CO) and Fe(Hfr)$_2$(cnpy)(bzlnc) was not successful, since they were very photosensitive. The bzlnc complexes were too stable in the dark to study the dissociation process of bzlnc at 25 °C.

The data of the visible spectra are shown in Table 2. The assignments of the bands for the bis(base) complexes were reported previously.[17,22–25] The bands at longer and shorter wavelengths were assigned to charge transfers from iron to α-diketone dioxime and from iron to pyridine ring, respectively. The bis(base) complexes of meim, im, buam, and pip did not exhibit the second band. The first band shifted to longer wavelengths with increasing basicity of the axial base. The axial ligation of CO and bzlnc, being good π-acceptors, gave rise to a band at short wavelength, and the position was not much affected by trans base. This may mean that the band in the CO and bzlnc complexes can be assigned to charge transfer from iron to CO and to bzlnc, respectively.

The infrared stretching frequencies for the CO and bzlnc complexes are given in Table 3. The CO stretches in the CO complexes occurred at lower wave numbers than that for free CO ($\nu_{\mathrm{CO}}=2143$ cm^{-1}). The ν_{CO} for the H$_2$dg complexes was smaller (by ≈ 20 cm^{-1}) than that for the H$_2$fr complexes. If we consider the ν_{CO} for the CO complexes as an indication of the ability of the π back-donation from iron to

TABLE 2. ABSORPTION MAXIMA OF VISIBLE SPECTRA OF OCTAHEDRAL BIS(2,2′-DIFURYLGLYOXIMATO)IRON(II) AND BIS(DIMETHYLGLYOXIMATO)IRON(II) COMPLEXES

Compound	λ/nm (10^{-3} ε)			
	L=base		L=CO	L=bzlnc
Fe(Hfr)$_2$(dmnpy)(L)	330 (29.2)	610 (19.1)	440 (16.6)	—
Fe(Hfr)$_2$(3,4-me$_2$py)(L)	369 (13.4)	578 (23.8)	435 (18.5)	—
Fe(Hfr)$_2$(4-mepy)(L)	370 (12.5)	576 (23.6)	437 (17.9)	494 (22.2)
Fe(Hfr)$_2$(py)(L)	380 (9.3)	568 (22.9)	436 (17.1)	494 (19.6)
Fe(Hfr)$_2$(4-clpy)(L)	398 (8.7)	561 (21.2)	436 (16.0)	—
Fe(Hfr)$_2$(acpy)(L)	514[a] (15.4)	554 (24.3)	436 (17.4)	—
Fe(Hfr)$_2$(3-clpy)(L)	406 (7.8)	555 (22.7)	436 (17.4)	491 (21.7)
Fe(Hfr)$_2$(cnpy)(L)	512[a] (16.9)	542 (21.8)	437 (15.2)	488 (18.7)
Fe(Hfr)$_2$(2,6-me$_2$py)(L)	380 (9.7)	571 (22.4)	435 (17.8)	—
Fe(Hfr)$_2$(2,4-me$_2$py)(L)	370 (11.6)	575 (21.4)	435 (16.9)	—
Fe(Hfr)$_2$(2-mepy)(L)	380 (9.2)	567 (22.6)	435 (17.3)	—
Fe(Hfr)$_2$(pip)(L)	—	606 (23.0)	445 (17.3)	—
Fe(Hfr)$_2$(buam)(L)	—	592 (23.0)	439 (20.9)	499 (20.9)
Fe(Hfr)$_2$(meim)(L)	—	591 (18.4)	434 (14.0)	494 (19.4)
Fe(Hfr)$_2$(im)(L)	—	589 (20.1)	431 (16.4)	493 (21.6)
Fe(Hdg)$_2$(py)(L)	410 (7.7)	511 (8.7)	391 (4.0)	—
Fe(Hdg)$_2$(meim)(L)	—	529 (7.8)	388 (4.5)	—

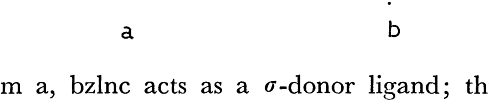
Solvent: chloroform. a) Shoulder.

TABLE 3. INFRARED FREQUENCIES OF CO AND NC IN CARBONYL AND BENZYL ISOCYANIDE COMPLEXES

Compound[a]	$\tilde{\nu}$/cm^{-1}			
	py	meim	3-clpy	buam
Fe(Hfr)$_2$(X)(CO)	2013	2010	2027	
Fe(Hdg)$_2$(X)(CO)	1988	1990		
Fe(Hfr)$_2$(X)(bzlnc)	2165	2162	2179	2161
Fe(Hdg)$_2$(X)(bzlnc)	2146	2142		

a) X=base.

CO, the H$_2$dg systems are seen to better than the H$_2$fr systems. This is expected, based on the greater inductive effect of the methyl group compared with that of the furyl group. The ν_{CO} values of the 3-clpy complexes were larger (by ≈15 cm^{-1}) than those of the py and meim complexes, which means that the strength of σ-donor property of trans base also affects significantly the π-bonding between iron and CO. Behavior of the NC stretching frequencies of the bzlnc complexes was more complicated: The ν_{NC} values of the H$_2$fr complexes were larger and those of the H$_2$dg complexes smaller than that of free bzlnc (ν_{NC}=2153 cm^{-1}).[26] This seems to be related to the two resonance forms of isocyanides:



In form a, bzlnc acts as a σ-donor ligand; this type of bonding is characterized by a shift of the ν_{NC} to higher frequency upon complex formation. In form b, bzlnc acts as a π-acceptor; this type of bonding occurs preferably with transition metals by making a π back-donation from metal to the ligand.[27] Thus the behavior of ν_{NC} observed in this study shows that form a is dominant in the H$_2$fr complexes.

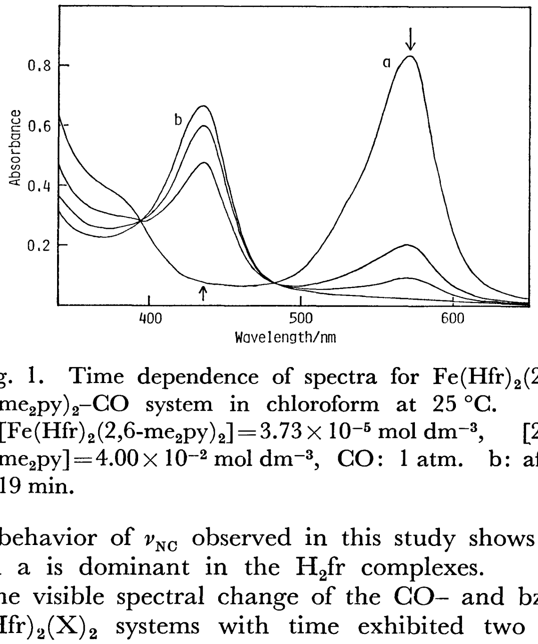


Fig. 1. Time dependence of spectra for Fe(Hfr)$_2$(2,6-me$_2$py)$_2$–CO system in chloroform at 25 °C. [Fe(Hfr)$_2$(2,6-me$_2$py)$_2$]$=3.73\times10^{-5}$ mol dm^{-3}, [2,6-me$_2$py]$=4.00\times10^{-2}$ mol dm^{-3}, CO: 1 atm. b: after 19 min.

The visible spectral change of the CO– and bzlnc–Fe(Hfr)$_2$(X)$_2$ systems with time exhibited two isosbestic points. As a typical example, the spectra of Fe(Hfr)$_2$(2,6-me$_2$py)$_2$–CO and Fe(Hfr)$_2$(2,6-me$_2$py)(CO)–2,6-me$_2$py systems are shown in Figs. 1 and 2. Two excellent isosbestic points were found at 394 and 481 nm, suggesting that the following reversible reaction takes place without oxidation of the bis(2,6-me$_2$py) complex:

$$\mathrm{Fe(Hfr)_2(X)_2 + L \underset{K}{\rightleftharpoons} Fe(Hfr)_2(X)(L) + X,} \qquad (1)$$

where X=base, L=CO or bzlnc, and K is an equilibrium constant. The reaction 1 is to pass through a five-coordinated intermediate (dissociative mechanism), as reported in other systems:

$$\mathrm{Fe(Hfr)_2(X)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(Hfr)_2(X) + X,} \qquad (2)$$

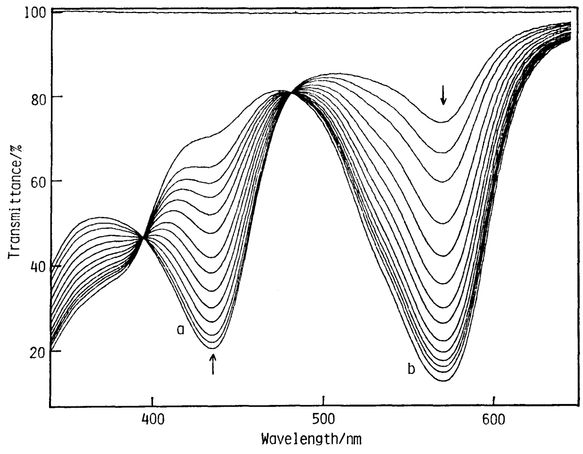


Fig. 2. Time dependence of spectra for $Fe(Hfr)_2(2,6\text{-}me_2py)(CO)$–2,6-$me_2py$ system in chloroform at 25 °C. $[Fe(Hfr)_2(2,6\text{-}me_2py)(CO)] = 4.03 \times 10^{-5}$ mol dm^{-3}, $[2,6\text{-}me_2py] = 7.25 \times 10^{-1}$ mol dm^{-3}. b: after 310 min.

$$Fe(Hfr)_2(X) + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(Hfr)_2(X)(L). \qquad (3)$$

If we assume a steady-state concentration for the five-coordinated intermediate and neglect k_{-2}, the CO or bzlnc complex-formation rate constant, k_{obsd}, can be represented by:

$$k_{obsd}^{-1} = (1/k_1)(1+(k_{-1}/k_2)([X]/[L])). \qquad (4)$$

Plots of k_{obsd}^{-1} *vs.* [X]/[CO] for several $Fe(Hfr)_2(X)_2$–CO systems are shown in Fig. 3. The solubility of CO in chloroform was taken as that in toluene at 25 °C (6.5×10^{-3} mol dm^{-3} atm^{-1}).[5,28] The plots for all the base systems gave good straight lines. The visible spectra of the $Fe(Hdg)_2(X)_2$–CO systems changed with an excellent isosbestic point. The plots of k_{obsd}^{-1} *vs.* [X]/[CO] gave also good straight lines (Fig. 4). The parameters k_1 and k_{-1}/k_2 were determined from the intercepts and the slopes. The intercept of pip in Fig. 3 and that of py in Fig. 4 were too small to allow us to estimate k_1.

The kinetic data were estimated by the least-squares method, and the equilibrium constants were calculated from the kinetic data. Several equilibrium constants were obtained experimentally and consistent with those calculated. The activation parameters were estimated from the kinetic data at 20, 25, and 30 °C.

The rate constants and the activation parameters for the $Fe(Hfr)_2(X)_2$–CO systems are given in Tables 4 and 5, respectively. Figure 5 shows the relationship between the rate constants and pK_a (K_a: dissociation constant of conjugate acid of the base). The $\log k_1$ values of the pyridines increased with decreasing basicity of the bases. But the $\log k_1$ values of cnpy and acpy were smaller and that of 2,6-me_2py was larger than predicted by their pK_a values. The imidazoles were more inert, and buam and pip more labile than predicted by their pK_a values. The sterically unhindered pyridines gave rise to ΔH_1^{*} values of the same degree in magnitude (≈ 105 kJ mol^{-1}).[29] The decreased ΔH_1^{*} value of 4-clpy may be due to the polymerizing property of the base.[30] The steric effect on the dissociation of the pyridines in the $Fe(Hfr)_2$ systems very little. The decreased ΔH_1^{*} values of the sterically hindered pyridines may support the steric hindrance by the methyl group in α position. The small steric effect is in striking contrast to that on dissociation of imidazoles in iron(II) phthalocyanine system, in which 2-methylimidazole is about 12700 times labile than

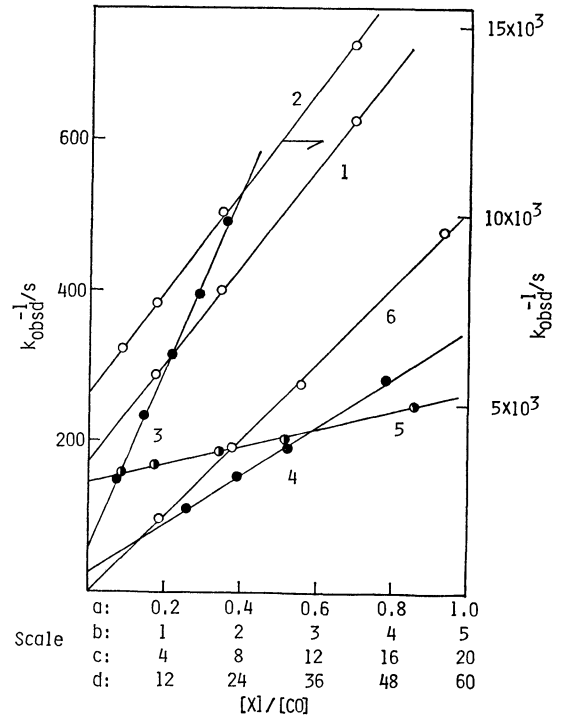


Fig. 3. Plots of k_{obsd}^{-1} *vs.* [X]/[CO] for $Fe(Hfr)_2(X)_2$–CO systems.
Scale a: X=py (1) and meim (2). Scale b: X=cnpy (3) and 3-clpy (4). Scale c: X=2,6-me_2py (5). Scale d: X=pip (6).

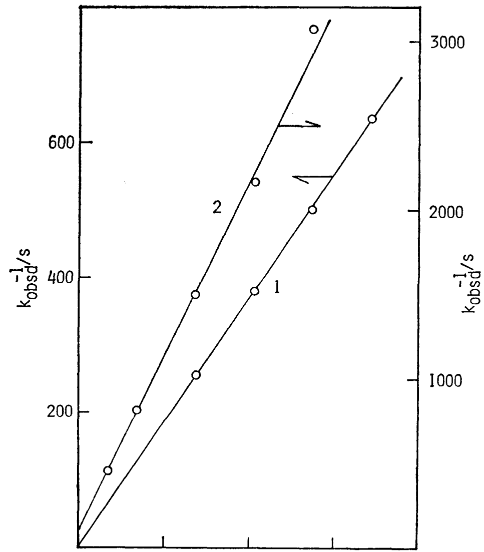


Fig. 4. Plots of k_{obsd}^{-1} *vs.* [X]/[CO] for $Fe(Hdg)_2(X)_2$–CO systems.
X=py (1) and meim (2).

Table 4. Rate constants of axial ligand dissociation for Fe(Hfr)$_2$(X)$_2$-CO system in chloroform at 25 °C

Base (X)	10^3k_1/s^{-1}	10^4k_{-2}/s^{-1}	k_{-1}/k_2	$K$$^{a)}$	
4-Dimethylaminopyridine	0.55±0.02	0.35±0.01	1.3	12	
3,4-Dimethylpyridine	3.36±0.03	0.736±0.005	2.3	20	
4-Methylpyridine	2.24±0.01	0.675±0.001	2.4	14	15$^{b)}$
Pyridine	5.2±0.3	1.06±0.05	3.1	16	18$^{b)}$
4-Chloropyridine	9.4±0.4	1.2±0.2	3.6	21	
3-Chloropyridine	37±5	1.77±0.05	2.3	91	32$^{b)}$
4-Acetylpyridine	4.53±0.05	1.23±0.05	3.1	12	
4-Cyanopyridine	16±2	2.1±0.1	3.7	21	25$^{b)}$
2,4-Dimethylpyridine	2.47±0.05	1.04±0.05	0.03	740	
2,6-Dimethylpyridine	6.83±0.08	1.23±0.05	0.04	1390	
2-Methylpyridine	5.7±0.4	1.12±0.05	0.05	1020	
1-Methylimidazole	0.178±0.005	0.192±0.005	2.5	4	
Imidazole	0.47±0.01	0.18±0.01	2.7	10	
Piperidine	>150	11.1±0.1	—	106$^{c)}$	
Butylamine	5.3±0.2	1.8±0.2	1.5	20	

a) Calculated from k_1, k_{-2} and k_{-1}/k_2. b) Obtained experimentally. c) Calculated from $k_{-1}/(k_1k_2)$ and k_{-2}.

Table 5. Activation parameters of axial ligand dissociation reactions in Fe(Hfr)$_2$(X)$_2$-CO systems at 25 °C

Base (X)	ΔH_1^* / kJ mol^{-1}	ΔS_1^* / J mol^{-1} K^{-1}	ΔH_{-2}^* / kJ mol^{-1}	ΔS_{-2}^* / J mol^{-1} K^{-1}
4-Dimethylaminopyridine	105±5	46±17	103±7	15±23
3,4-Dimethylpyridine	106±2	64±7	106±2	30±7
4-Methylpyridine	102±2	46±8	105±2	25±8
Pyridine	106±2	67±8	108±7	42±25
4-Chloropyridine	75±8	−33±33	100±4	13±13
3-Chloropyridine	107±10	85±33	108±2	46±8
4-Acetylpyridine	95±6	28±19	100±2	15±5
4-Cyanopyridine	90±2	21±8	92±8	−2±29
2,4-Dimethylpyridine	103±5	26±8	100±8	7±28
2,6-Dimethylpyridine	97±9	19±15	100±7	16±23
2-Methylpyridine	90±2	13±6	106±1	34±4
1-Methylimidazole	112±2	50±8	109±10	17±33
Imidazole	120±3	93±11	110±3	34±11
Piperidine	—	—	95±11	17±38
Butylamine	103±2	59±8	105±4	33±13

Solvent: chloroform.

imidazole.[2] The dissociation of 1,2-dimethylimidazole in Fe(Hfr)$_2$ system also was too fast to study on a conventional spectrophotometer. Therefore, it seems that the steric effect for both systems may be affected by the difference in rigidity of the macrocycles as well as by some difference in the axial ligation property of pyridine and imidazole. π-Receptive groups such as cyano and acetyl groups in pyridine ring decreased the ΔH_1^* value. If we consider ΔH_1^* as the binding energy between iron and base, the π-receptive groups in pyridine ring are seen to weaken the bond between iron and base. The ΔS_1^* values of cnpy, acpy and the sterically hindered pyridines were rather small, as compared with those of the other pyridines. The increased lability of buam and pip may be attributed to the inability of those bases to undergo dπ-π interaction, in addition to the steric repulsion in the pip system.[31] The imidazoles were more inert and gave rise to larger ΔH_1^* values than the pyridines. This may be explained in terms of π-basicity of the imidazoles,[32] although we could not find good evidence of the dπ-π interaction between iron and imidazole ring in the infrared data of the CO and bzlnc complexes.

The log k_2 values of the sterically unhindered pyridines also increased slightly with decreasing basicity of the bases. The sterically hindered pyridines allowed CO to be a little more labile than predicted by their pK_a values. The small steric effect is in striking contrast to the results for imidazole systems of iron(II) phthalocyanine and chelated hemes, in which 2-methylimidazole allows CO to be about 20 times more labile than imidazole.[2,14] The CO in the imidazole systems was 5 times more inert and the CO in the pip system 10 times more labile than that in the py system. The sterically unhindered pyridines

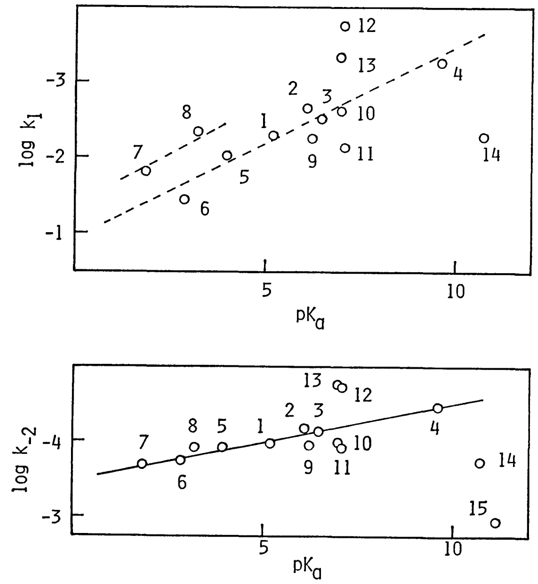


Fig. 5. Plots of $\log k_1$ and $\log k_{-2}$ *vs.* pK_a.
1: py, 2: 4-mepy, 3 3,4-me$_2$py, 4: dmnpy, 5: 4-clpy, 6: 3-clpy, 7: cnpy, 8: acpy, 9: 2-mepy, 10: 2,4-me$_2$py, 11: 2,6-me$_2$py, 12: meim, 13: im, 14: buam, 15: pip.

gave rise to ΔH^{*}_{-2} values of the same degree in magnitude ($\approx$105 kJ mol^{-1}), which were roughly equal to the ΔH_1^{*} values. The ΔH^{*}_{-2} values of the sterically hindered pyridines and those of cnpy and acpy, being π-acceptors, were smaller than 105 kJ mol^{-1}. If factors favoring π back-donation facilitate electron transfer from metal to ligand, π-receptive bases are expected to weaken the dπ-π interaction between iron and CO. This is presumably supported by the small ΔH^{*}_{-2} values of cnpy and acpy. The ΔH^{*}_{-2} values of the imidazoles were slightly larger and the ΔH^{*}_{-2} value of pip smaller than that of py. The ΔS^{*}_{-2} values were smaller than the corresponding ΔS_1^{*} values, which results in greater inertness of CO compared with that of the bases. The bases used in this study are strong dipoles (1.2 D for pip—4.3 D for dmnpy), and the five-coordinated intermediate assumed here may have an electric dipole moment (complex dipole moment) along the direction of axial ligand since the iron in the intermediate is found to lie out of the plane of the equatorial ligands. Therefore, it is expected that the activation potential for a dissociative process of base may be contributed to some extent by the long range electrostatic repulsion between the base dipole and the induced complex dipole.[33] On the other hand, the electric dipole moment of CO is very small (0.1 D), suggesting that the activation potential for the dissociation process of CO may be greatly contributed by a short range electron-exchange interaction between iron and CO. If we assume that the Δr $(=r^{*}-r_0)$ value for a dissociation of base is larger than that for the dissociation of CO, where r_0 and r^{*} are the distances between iron and the leaving ligand in the initial complexes and their transition states, and that the activation entropy is due partially to the Δr values, the dissociation of bases may give rise to larger ΔS^{*} than that of CO. This rough estimation is consistent with the results obtained in this study.

The dissociation rates of CO in the Fe(Hfr)$_2$ systems did not correlate with the CO stretching frequencies in Table 3, as found in heme systems previously.[34] This suggests that both σ electron donation and π back-donation contribute to the stability of CO complexes, but the CO stretching frequency is sensitive to changes in the π back-donation of CO complexes.

The k_{-1}/k_2 ratios obtained in this study are comparable in magnitude to those for iron(II) phthalocyanine and iron(II) diphenylglyoxime systems.[2,19] On the other hand, the ratio for the sterically hindered pyridine systems was far too small. The steric effect on k_{-1}/k_2 ratio is presumably related to the structure of the five-coordinated intermediate. The result of k_{-1}/k_2 ratio in the pyridine systems is also in striking contrast to that in imidazole systems of iron(II) phthalocyanine, where the ratio of 2-methylimidazole is comparable to that of imidazole.[2] The values of equilibrium constant, K, estimated in this study were roughly equal in magnitude. But the K values of the sterically hindered pyridines were much larger; this resulted from the decreased k_{-1}/k_2 ratio.

The rate constants and the activation parameters for the Fe(Hdg)$_2$(X)$_2$–CO systems are given in Table 6. The Fe(Hdg)$_2$ systems gave rise to k_1 values about 50 times larger than those in the Fe(Hfr)$_2$ systems. The CO in the Fe(Hdg)$_2$ complexes was about twice as inert as that in the Fe(Hfr)$_2$ complexes. The ΔH_1^{*} value of Fe(Hdg)$_2$(meim)$_2$ was smaller than that of Fe(Hfr)$_2$(meim)$_2$, but the ΔH^{*}_{-2} and ΔS^{*}_{-2} values of Fe(Hdg)$_2$(py)(CO) were larger than those of Fe(Hfr)$_2$(py)(CO). The change of the ΔH_1^{*} values suggests that the bond between iron and axial base (mainly σ bond) in Fe(Hdg)$_2$ complexes is weaker than that in Fe(Hfr)$_2$ complexes, as expected by the greater inductive effect of methyl group than that of furyl group. The result that the dissociation of CO is not much affected by the electronic effect of the substituents is consistent with that reported recently in some chelated hemes.[5] These suggest that stability of CO complexes is determined by both σ electron donation and π back-donation. The increased ΔH^{*}_{-2} value

TABLE 6. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR AXIAL LIGAND DISSOCIATION IN Fe(Hdg)$_2$(X)$_2$-CO SYSTEMS AT 25 °C

Base (X)	10^3k_1/s^{-1}	10^4k_{-2}/s^{-1}	k_{-1}/k_2	K	ΔH^{*} / kJ mol^{-1}	ΔS^{*} / J mol^{-1} K^{-1}
Pyridine	>120	0.401±0.005	—	680$^{a)}$	$\Delta H^{*}_{-2}=131\pm4$	$\Delta S^{*}_{-2}=112\pm13$
1-Methylimidazole	10.3±0.6	0.119±0.005	2.1	410$^{b)}$	$\Delta H_1^{*}=104\pm9$	$\Delta S_1^{*}=66\pm29$

Solvent: chloroform. a) Calculated from $k_{-1}/(k_1k_2)$ and k_{-2}. b) Calculated from k_1, k_{-2}, and k_{-1}/k_2.

TABLE 7. RATE CONSTANTS OF AXIAL LIGAND DISSOCIATION FOR $Fe(Hfr)_2(X)_2$–bzlnc SYSTEMS AT 25 °C

Base (X)	$10^3k_1/s^{-1}$	k_{-1}/k_2
Pyridine	4.9 ± 0.3	1.1
4-Methylpyridine	2.24 ± 0.01	0.9
3-Chloropyridine	46 ± 18	0.8
4-Cyanopyridine	17 ± 2	1.3
1-Methylimidazole	0.183 ± 0.001	0.8
Imidazole	0.48 ± 0.01	—
Butylamine	5.6 ± 0.2	0.5

of $Fe(Hdg)_2(py)(CO)$ is presumably due to better ability of π back-bonding formation of $Fe(Hdg)_2$ complexes, as concluded on the basis of the infrared data.

The rate constants for several $Fe(Hfr)_2(X)_2$–bzlnc systems are summarized in Table 7. The k_1 values for the $Fe(Hfr)_2(X)_2$–bzlnc systems were in agreement with those for the $Fe(Hfr)_2(X)_2$–CO systems; this is good evidence of the dissociative mechanism assumed in this study. The k_{-1}/k_2 ratios for the bzlnc systems were 1/3 in magnitude, compared with those for the corresponding CO systems. This means that the k_2 values of the bzlnc systems are 3 times larger than those of the CO systems. The bzlnc complexes were much more stable than the CO complexes.

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References

1) D. V. Stynes and B. R. James, *J. Chem. Soc., Chem. Commun.*, **1973**, 325.

2) D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, **96**, 2733 (1974).

3) C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 6707 (1975).

4) D. A. Sweigart, *J. Chem. Soc., Dalton Trans.*, **1976**, 1476.

5) B. R. James, K. J. Reimer, and T. C. T. Wong, *J. Am. Chem. Soc.*, **99**, 4815 (1977).

6) D. V. Stynes, *Inorg. Chem.*, **16**, 1170 (1977).

7) I. W. Pang and D. V. Stynes, *Inorg. Chem.*, **16**, 2192 (1977).

8) J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, **1978**, 1709.

9) D. E. Hamilton, T. J. Lewis, and N. K. Kildahl, *Inorg. Chem.*, **18**, 3364 (1979).

10) C. E. Holloway, D. V. Stynes, and C. P. J. Vuik, *J. Chem. Soc., Dalton Trans.*, **1979**, 124.

11) J. Martinsen, M. Miller, D. Trojan, and D. A. Sweigart, *Inorg. Chem.*, **19**, 2162 (1980).

12) C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi, and M. Brunori, *J. Chem. Soc., Dalton Trans.*, **1981**, 1120.

13) J. Geibel, J. Cannon, D. Campbell, and T. G. Traylor, *J. Am. Chem. Soc.*, **100**, 3575 (1978).

14) D. K. White, J. B. Cannon, and T. G. Traylor, *J. Am. Chem. Soc.*, **101**, 2443 (1979).

15) T. G. Traylor, D. K. White, D. H. Campbell, and A. P. Berzinis, *J. Am. Chem. Soc.*, **103**, 4932 (1981).

16) D. Lavalette, C. Tetreau, and M. Momentear, *J. Am. Chem. Soc.*, **101**, 5395 (1979).

17) B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, **1958**, 462.

18) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Am. Chem. Soc.*, **94**, 727 (1972).

19) L. Vaska and T. Yamaji, *J. Am. Chem. Soc.*, **93**, 6673 (1971).

20) I. W. Pang and D. V. Stynes, *Inorg. Chem.*, **16**, 590 (1977).

21) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

22) Y. Sasaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **58**, 244 (1980).

23) N. Sanders and P. Day, *J. Chem. Soc., A*, **1969**, 2303.

24) C. Matsumoto, Y. Yamane, and K. Shinra, *Nippon Kagaku Zasshi*, **89**, 44 (1968).

25) Y. Yamane, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jpn.*, **44**, 1581 (1971).

26) The ν_{NC} value for free bzlnc is slightly larger than that reported in Ref. 21.

27) F. Millich, *Chem. Rev.*, **72**, 101 (1972).

28) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed, D. Van Nostrand Co., New York, N.Y. (1970), Vol. 1, p. 218.

29) The activation parameters of 3-clpy differ from the data in the preliminary report (*Chem. Lett.*, **1981**, 1117). The difference may be due to impurities in 3-clpy.

30) H. S. Mosher, "Heterocyclic Compounds," ed by R. C. Elderfield, Wiley, New York (1950), Vol. 1, p. 516.

31) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2073 (1972).

32) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 8477 (1973).

33) The existence of such an electrostatic repulsion may be supported by the result that the rate constants for association of the pyridines in chelated heme systems are correlated to the electric dipole moments of the bases, where one base B (imidazole or pyridine) is covalently linked to the TPP macrocycle (Fe(II)TPP-B). See Ref. 16.

34) C. K. Chang and D. Dolphin, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 3338 (1976).