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INFLUENCE OF BASICITY OF AXIAL LIGANDS ON REACTIONS OF BIS(α-FURILDIOXIMATO)IRON(II) WITH CARBON MONOXIDE

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Reactions of bis(α-furildioximato)iron(II), $Fe(FrH)_2(X)_2$, (X= pyridine, 4-cyanopyridine, 3-chloropyridine, 4-chloropyridine, 4-methylpyridine, 1-methylimidazole and butylamine) with carbon monoxide was studied kinetically in chloroform solutions. The reactions proceeded reversibly through a dissociative mechanism. The axial ligand-dissociation rate constants and the activation parameters of $Fe(FrH)_2(X)_2$ and $Fe(FrH)_2(X)(CO)$ were determined and discussed in terms of basicity of bases (X).

It is well-known that axial ligands of six-coordinate iron(II) porphyrins are labile in spite of their diamagnetism. The enhanced lability plays an important role in functions of heme proteins. Therefore, many investigators have recently interested in studies of axial ligand exchange reactions of metal complexes with planar macrocyclic ligands. All of the systems studied so far undergo the reactions through a dissociative mechanism. Bis(α-dioximato)iron(II) possesses a similar structure to iron(II) porphyrins and is able to bind carbon monoxide and isocyanides reversibly.[1-3] In this work, the author studied the reactions of bis(α-furildioximato)iron(II) with carbon monoxide in order to reveal the basicity effect of axial ligands on the reactions.

Bis(α-furildioximato)iron(II), $Fe(FrH)_2(X)_2$, (X= 4-cyanopyridine, 3-chloropyridine, pyridine, 4-methylpyridine and 1-methylimidazole) were synthesized according to the procedures described previously.[4)] $Fe(FrH)_2(buam)_2$ (buam= butylamine) and $Fe(FrH)_2(4\text{-}Clpy)_2$ (4-Clpy= 4-chloropyridine) solutions were prepared by dissolving $Fe(FrH)_2(py)_2$ and $Fe(FrH)_2(3\text{-}Clpy)_2$, respectively in chloroform which contained large excess of the bases. Measurements of absorbance were made on a Hitachi 323 automatic recording spectrophotometer, being equipped with a thermostated cell-holder and connected with a vacuum line.

The complexes above exhibited charge transfer bands (ε= ca. 20,000 $cm^{-1}M^{-1}$) in the range of 540-590 nm. Under a CO atmosphere, the bands shifted to about 440 nm. As an example, the spectral change of $Fe(FrH)_2(py)_2$-CO system is shown in Fig.1. Two isosbestic points are found at 396 and 481 nm, suggesting that pyridine-carbonyl complex forms according to the following reaction:

$$Fe(FrH)_2(X)_2 + CO \underset{K}{\rightleftharpoons} Fe(FrH)_2(X)(CO) + X. \qquad (1)$$

The carbonyl complex, $Fe(FrH)_2(py)(CO)$, was obtained as a brown crystal from the reaction mixture of $Fe(FrH)_2(py)_2$ and CO in dichloromethane by the addition of

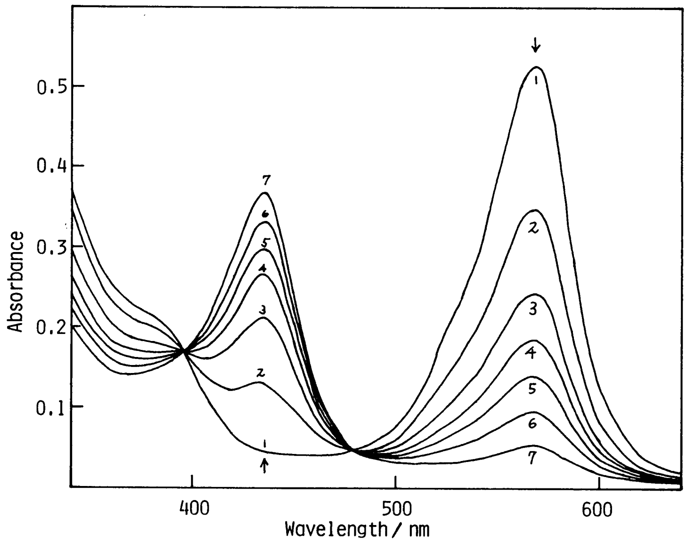

Fig. 1. Time dependence of spectra of $Fe(FrH)_2(py)_2$-CO system in chloroform at 25 °C. $[Fe(FrH)_2(py)_2]=2.31\times10^{-5}M$, $[py]=9.95\times10^{-3}M$, CO: 1 atm., and cell-length=1 cm.

petroleum ether. (Calcd for $C_{26}H_{19}N_5O_9Fe$: C, 51.93%; H, 3.19%; N, 11.65%. Found: C, 51.92%; H, 3.22%; N, 11.45%.)

The reaction of bis(α-furildioximato)iron(II) with CO is thought to proceed via the following dissociative mechanism:

$$Fe(FrH)_2(X)_2 \xrightleftharpoons[k_{-1}]{k_1} Fe(FrH)_2(X) + X \qquad (2)$$

$$Fe(FrH)_2(X) + CO \xrightleftharpoons[k_{-2}]{k_2} Fe(FrH)_2(X)(CO). \qquad (3)$$

Usually the six-coordinate complexes are diamagnetic,[5,6] but the five-coordinate one is probably of a high or an intermediate spin state, suggesting that k_{-1} and k_2 would be far larger than k_1 and k_{-2}. Thus, if we can assume a steady-state concentration for the five-coordinate intermediate and neglect k_{-2}, the above reactions (2) and (3) can be regarded as the pseudo-first-order reaction, and the carbonyl complex-formation rate constant (k_{obs}) can be represented by:

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

Plots of the k_{obs}^{-1} vs. [X]/[CO] are shown in Fig. 2. The solubility of CO in chloroform was taken as that in toluene at 25 °C (6.5×10^{-3} M atm^{-1}). $Fe(FrH)_2(X)(CO)$ samples were prepared in chloroform under a CO atmosphere, N_2 gas being bubbled through for 2 min. The measurements for k_{-2} were carried out in the solvent containing large excess of the bases ($[X]>10^{-1}$ M). The k_{-2} value of $Fe(FrH)_2(py)(CO)$ was consistent with that of the isolated pyridine-carbonyl complex in pyridine. The carbonyl complexes displayed a photochromism similar to hemoglobin and myoblobin.

The kinetic data estimated by the least-squares method and the equilibrium

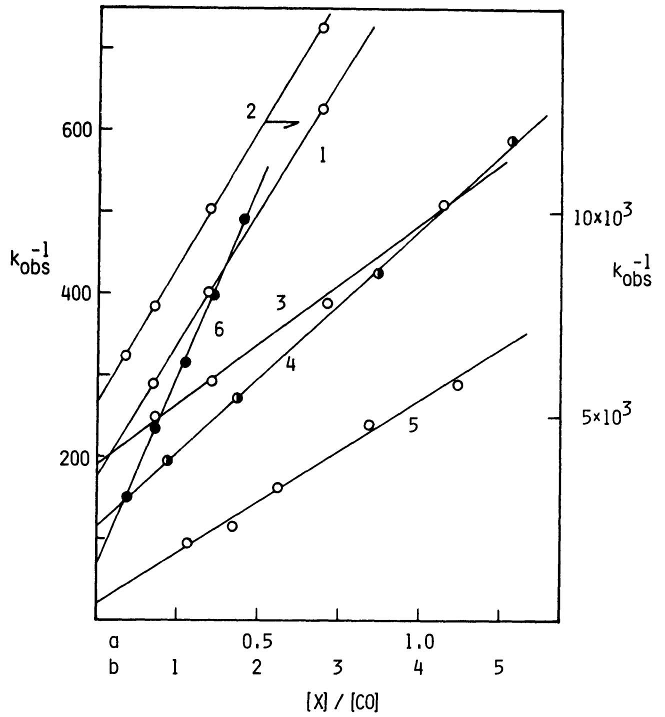

Fig. 2. Plots of k_{obs}^{-1} vs. [X]/[CO].
a: X= py (1), 1-meim (2), buam (3) and 4-Clpy (4)
b: X= 3-Clpy (5) and 4-CNpy (6)

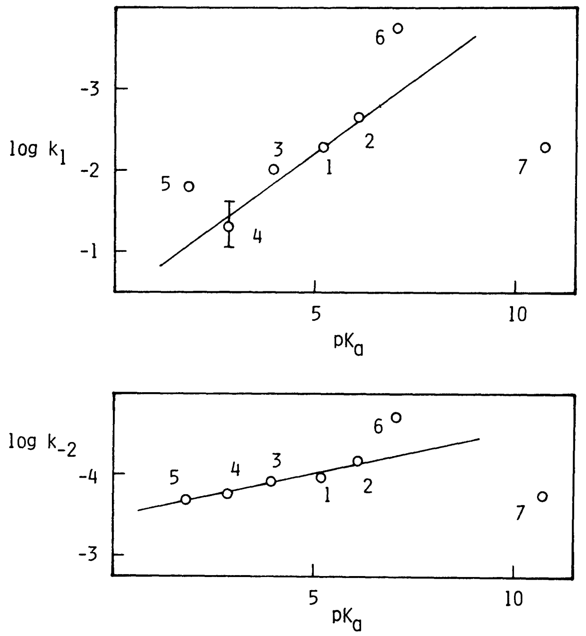

Fig. 3. Plots of log k_1 and log k_{-2} vs. pK_a.
1: py, 2: 4-mepy, 3: 4-Clpy,
4: 3-Clpy, 5: 4-CNpy, 6: 1-meim,
7: buam

constants calculated from the rate constants are shown in Tables 1 and 2. Several equilibrium constants were consistent with those obtained experimentally. The activation parameters were estimated from the kinetic data at 20, 25 and 30 °C and the absolute reaction rate equation where it was assumed that κ=1. Figure 3 shows a relationship between the rate constants and pK_a (K_a: dissociation constant of conjugated acids of the bases). The log k_1 values of the pyridines except 4-CNpy increased with lowering of basicity and the log k_1-pK_a plots displayed a linearity, but the plots of 1-meim and buam deviated from the linear relationship. A similar tendency

Table 1. Rate Constants of Axial Ligand Dissociation in Chloroform at 25 °C

$Fe(FrH)_2(X)_2$-CO	10^3k_1 (s^{-1})	10^4k_{-2} (s^{-1})	k_{-1}/k_2	K	
$Fe(FrH)_2(py)_2$-CO	5.2±0.3	1.06±0.05	3.1	16	$18^{a)}$
$Fe(FrH)_2$(4-mepy)$_2$-CO	2.24±0.01	0.675±0.001	2.4	14	$15^{a)}$
$Fe(FrH)_2$(4-Clpy)$_2$-CO	9.4±0.4	1.2±0.1	3.6	21	
$Fe(FrH)_2$(3-Clpy)$_2$-CO	51±28	1.77±0.05	3.2	90	
$Fe(FrH)_2$(4-CNpy)$_2$-CO	16±2	2.1±0.1	3.7	21	$25^{a)}$
$Fe(FrH)_2$(1-meim)$_2$-CO	0.178±0.005	0.192±0.005	2.5	3.7	
$Fe(FrH)_2(buam)_2$-CO	5.3±0.2	1.8±0.2	1.5	20	

a): Data obtained from equilibrium experiments

Table 2. Activation Parameters of the Axial Ligand Dissociation Reactions in Chloroform at 25 °C

$Fe(FrH)_2(X)_2$-CO	$\Delta H^{\ddagger}_{1}$ (kJ/mol)	$\Delta S^{\ddagger}_{1}$ (J/mol K)	$\Delta H^{\ddagger}_{-2}$ (kJ/mol)	$\Delta S^{\ddagger}_{-2}$ (J/mol K)
$Fe(FrH)_2(py)_2$-CO	106±2	67±8	108±7	42±25
$Fe(FrH)_2$(4-mepy)$_2$-CO	102±2	46±8	105±2	25±8
$Fe(FrH)_2$(4-Clpy)$_2$-CO	75±8	-33±33	100±4	13±13
$Fe(FrH)_2$(3-Clpy)$_2$-CO	——	——	108±2	46±8
$Fe(FrH)_2$(4-CNpy)$_2$-CO	90±2	21±8	92±8	-2±29
$Fe(FrH)_2$(1-meim)$_2$-CO	112±2	50±8	109±10	17±33
$Fe(FrH)_2(buam)_2$-CO	103±2	59±8	105±4	33±13

was also observed in the dissociation of CO trans to the bases. These results are resemble to relationships between 1:1 adduct-formation constants of iron(II) and cobalt(II) porphyrins with N-bases and the basicity,[7,8] suggesting that the π-rings of the bases play some role in interaction between a central iron(II) and axial ligands. The activation parameters for the reactions studied in this work give some interesting informations. It can be expected that lowering of basicity of axial ligands would result in rather small bond energy between an iron(II) and ligands. In fact, temperature dependency of k_1 for $Fe(FrH)_2$(3-Clpy)$_2$ was too small that we could not estimate the activation parameters. Whereas, $Fe(FrH)_2$(4-CNpy)$_2$ displayed considerably small k_1 and large $\Delta H^{\ddagger}_{1}$. Furthermore, the $\Delta H^{\ddagger}_{-2}$ of $Fe(FrH)_2$-(4-CNpy)(CO) was 92 kJ/mol, but those of the other carbonyl complexes were about 105 kJ/mol. The results suggest that 4-CNpy, which is a very strong π-acceptor, can take a relatively strong bond with the central iron(II) ion through a dπ-π interaction mechanism and weaken the interaction of CO with the iron(II) ion in the carbonyl complex through the mechanism.

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