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Kinetic and Thermodynamic Characterization of Thermal Pyridine Liberation-Anation Reactions of Bis(2,3-alkanedione dioximato)dipyridinecobalt(III) Iodide in the Solid State

Setsuko KINOSHITA,* Hisanobu WAKITA, and Isao MASUDA
Department of Chemistry, Faculty of Science, Fukuoka University,
Nanakuma, Jonan-ku, Fukuoka 814-01

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Thermodynamic and kinetic characterizations were carried out on the thermal, pyridine liberation-anation reactions, $[Co^{III}(R,CH_3\text{-dioxH})_2(py)_2]I \xrightarrow{\Delta} [Co^{III}(R,CH_3\text{-dioxH})_2(py)I]+py\uparrow$.* These occurred endothermally in the solid state of the complexes. The ΔH values of the reactions were determined. A large increment in the entropy was found to be indispensable for the progress of the reactions; it could be brought about by the liberation of gaseous pyridine from the solid system of the complexes. The kinetic analyses revealed that the reaction rates were increased by the substitution of R with the longer-carbon-chain alkyl groups. The activation enthalpies and activation free energies were shown to be decreased by the above substitutions. The Co^{III}-pyridine bond was observed to be weakened by the electron-donating inductive effect of R to the central cobalt atom and by the steric interference of R toward axial pyridine coordination.

Tsuchiya *et al.* have revealed that the complexes, $[Ni(H_2O)_2(N,N'\text{-deen})_2]Cl_2$* and $[Cr(NH_3)_6]X_3$ ($X=Cl^-$, Br^-), thermally liberate the volatile ligands in the coordination sphere such as H_2O or NH_3 accompaning anation reactions, in the solid state.1) Analogous anation reactions which occur in the solid state were investigated by Zsakó *et al.* using complexes of the type, $[Co(DH)_2B_2]X$ [DH=dimethylglyoximato and (*E,E*)-(benzil dioximato); B=pyridine, aniline and their derivatives; $X=Cl^-$, Br^-, I^-, and SCN^-]; these thermally eliminated B to produce complexes of the type, $[Co(DH)_2(B)X]$.2) Although they carried out kinetic analyses on these reactions, they only achieved ambiguous conclusions, probably due to their indiscriminate choice of the compounds.

In the present article, complexes of 2,3-alkanedione dioximes, $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$,* with a series of extended alkyl groups R on the dioximato moiety, have been subjected to thermal investigation. The steric effect on the reactions arising from the alkyl groups will be discussed. In our previous investigation, it was revealed that the thermally induced one-electron transfer reactions from ligand L to Co^{III} in the solid $[Co^{III}(salen)L]$ complexes (L=2,4-alkanedionato ligand) were controlled dominantly by the activation entropies which were increased by the substitution of alkyl groups on the carbon atom at the 4-position of L.3)

Experimental

Materials. The ligands, $R,CH_3\text{-dioxH}_2$, were prepared as described elsewhere.4) The series of $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$ complexes, including newly prepared ones with $R=C_2H_5$, $n\text{-}C_3H_7$, and $n\text{-}C_4H_9$, were prepared by following the method reported in the literature.5) The complexes were recrystallized from dichloromethane solution by addition of petroleum ether to the solution. The analytical data of the complexes are given in Table 1. As Table 1 shows, the complexes were obtained in an anhydrous state when they included $R=CH_3$ and C_2H_5, but were obtained dihydrate and tetrahydrate when they included $R=n\text{-}C_3H_7$ and $n\text{-}C_4H_9$, respectively.

TABLE 1. ANALYTICAL DATA OF THE COMPLEXES, $[Co(R, CH_3\text{-dioxH})_2(py)_2]I$a)

R	C %	H %	N %	Co %
CH_3	37.61	4.14	14.48	10.38
	(37.66)	(4.18)	(14.65)	(10.26)
C_2H_5	40.04	4.53	13.94	9.89
	(39.87)	(4.32)	(13.96)	(9.79)
$n\text{-}C_3H_7$; dihydrate	39.65	5.41	12.62	8.84
	(39.46)	(5.79)	(12.15)	(8.80)
$n\text{-}C_4H_9$; tetrahydrate	39.46	6.03	11.51	8.07
	(39.76)	(5.94)	(11.19)	(8.03)

a) Calculated values are given in parentheses.

The ^1H NMR spectra in DMSO-d_6 solution showed that all the complexes obtained here have a peak at 18.18 ppm which could be ascribed to the hydrogen atom in the =N-O-H-O-N= group formed by an intramolecular hydrogen bond in the complex molecules.6) This is consistent with the assumption that the two dioximate monoanion molecules are coordinated symmetrically in the equatorial plane and the two pyridine molecules, in the axial positions.

Measurements. TG-DSC and powder X-ray diffraction measurements were carried out as described previously.4) The kinetic analyses under isothermal conditions were carried out on the TG curves. The particle size of the samples provided for the thermal analyses was under 200 mesh.

Results

Pyrolysis. The TG-DSC curves are shown in Fig. 1. For the $[Co(CH_3,CH_3\text{-dioxH})_2(py)_2]I$ complex, an endothermic DSC peak appeared with a maximum at 158 °C, and a weight-loss corresponded to this change was 13.7%, being in agreement with calculated 13.8% for the elimination of one mole of pyridine per mole of complex. The powder X-ray diffraction of the product which was left behind after the above weight-loss was coincident with that of authentic [Co(CH3,CH3-

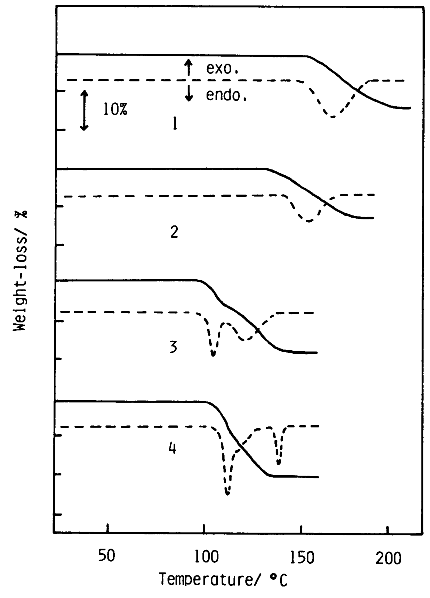

Fig. 1. TG(——) and DSC(----) curves of the complexes, $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$, in a flowing N_2 atmosphere. Heating rate: 10 °C/min.

1, $R=CH_3$; 2, $R=C_2H_5$; 3, $R=n\text{-}C_3H_7$ (dihydrate); 4, $R=n\text{-}C_4H_9$ (tetrahydrate).

$dioxH)_2(py)I]$.[7] Similarly, $[Co(C_2H_5,CH_3\text{-dioxH})_2(py)_2]I$ released pyridine leaving behind $[Co(C_2H_5,CH_3\text{-dioxH})_2(py)I]$. The observed weight-loss, 13.1%, corresponded to the calculated value, 13.1%. For $[Co(n\text{-}C_3H_7,CH_3\text{-dioxH})_2(py)_2]I\cdot 2H_2O$, dehydration occurred at *ca.* 100 °C, the weight-loss was 5.7% (Calcd, 5.4%). Then, pyridine was liberated; the weight-loss was 12.8% (Calcd, 12.5%). In the case of $[Co(n\text{-}C_4H_9,CH_3\text{-dioxH})_2(py)_2]I\cdot 4H_2O$, dehydration occurred accompanied by subsequent pyridine liberation; the total weight-loss was 21.2% (Calcd, 20.7%). A DSC peak at 143 °C is due to the melting of the resulting $[Co(n\text{-}C_4H_9,CH_3\text{-dioxH})_2(py)I]$. The results of the above thermal analyses are consistent with the following reaction scheme:

$$[Co(R, CH_3\text{-dioxH})_2(py)_2]I \xrightarrow{\Delta} [Co(R, CH_3\text{-dioxH})_2(py)I] + py\uparrow. \qquad (1)$$

The reactions all proceeded endothermally. The enthalpy changes, ΔH values, determined by means of the DSC peak area measurement,[4] are given in Table 2.

Kinetic Analysis. As seen in Fig. 1, the pyridine liberation-anation reactions (Eq. 1) tend to occur at lower temperatures when the complexes include R having longer-carbon-chains. In order to reveal the kinetic character of the reactions, the kinetic analyses were carried out under isothermal conditions. It was found that the rate plots were linear. This is exemplyfied in Fig. 2 by the results obtained for $[Co(CH_3,CH_3\text{-dioxH})_2(py)_2]I$; similar linear relations were also obtained for the other complexes. These rate plots indicated that the reactions proceeded following the Avrami-Erofeev equation (Eq. 2),[8] for all the complexes.

$$\alpha/1-\alpha = kt^n \ (n=1) \qquad (2)$$

Table 2. Thermodynamic data of pyridine liberation-anation reactions of the complexes, $[Co(R, CH_3\text{-dioxH})_2(py)_2]I$

R	DSC peak maximum temp/K	ΔH kJ mol^{-1}	ΔS JK^{-1} mol^{-1}
CH_3	431	50 ± 2	$>116\pm5$
C_2H_5	427	47 ± 3	$>110\pm7$
$n\text{-}C_3H_7$	393	39 ± 2	$>99\pm5$

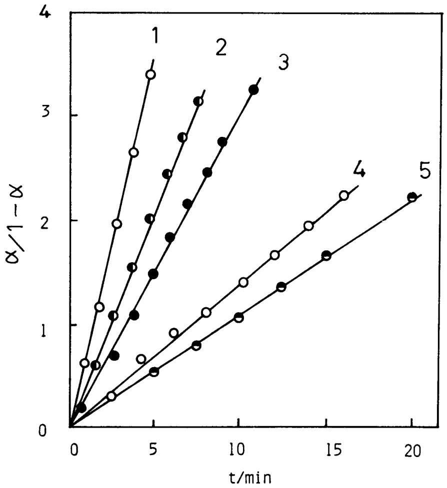

Fig. 2. Rate plots for pyridine liberation-anation reactions of $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$; $R=CH_3$, under isothermal conditions.

1, 422.7 K; 2, 419.0 K; 3, 416.7 K; 4, 413.9 K; 5, 411.6 K.

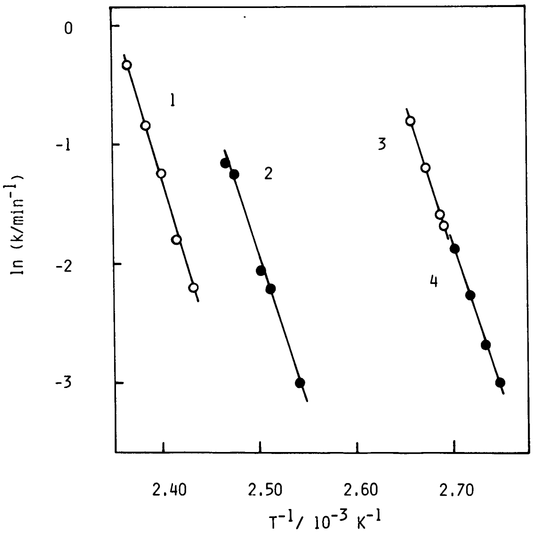

Fig. 3. Arrhenius plots for pyridine liberation-anation reactions of $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$.

1, $R=CH_3$; 2, $R=C_2H_5$; 3, $R=n\text{-}C_3H_7$; 4, $R=n\text{-}C_4H_9$.

In Eq. 2, α is the molar fraction of $[Co(R,CH_3\text{-dioxH})_2(py)I]$ produced in the system by the reaction (Eq. 1); k, the rate constant; t, the reaction time. The k values at several different temperatures were determined from the slopes of the straight lines in the rate plots. Then, the Arrhenius plots gave good linear relations as shown in Fig. 3. According to the Arrhenius equation, $k=A\exp(-E/RT)$, the activation energies, E values, and the pre-exponential factors, A valuse, were calculated from these Arrhenius plots. In order to disclose the reaction character more extensively, the activation enthalpies, ΔH^{*} values, and the activation entropies, ΔS^{*} values, were calculated by Eqs. 3 and 4, respectively:[3]

$$\Delta H^{*} = E - RT \tag{3}$$

$$\Delta S^{*} = R[\ln(Ah/kT)-1]. \tag{4}$$

The E value, 266±9 kJ mol^{-1}, obtained for [Co(CH_3,CH_3-dioxH)$_2$(py)$_2$]I is larger as compared with E=227 kJ mol^{-1} reported by Zsacó *et al.*,[2] who determined it under non-isothermal conditions.

Discussion

Thermodynamics. As described in the results section, the [Co(R,CH_3-dioxH)$_2$(py)$_2$]I complexes thermally liberated pyridine in the solid state to produce the [Co(R,CH_3-dioxH)$_2$(py)I] complexes (*cf.* Eq. 1). A thermodynamic cycle regarding the reactions is delineated in Fig. 4. As is seen in Fig. 4, the observed ΔH value is composed of those due to the three energy terms given in Eq. 5:

$$\Delta H = \Delta H_{\text{subst}} + (\Delta H_{\text{lattice}} - \Delta H'_{\text{lattice}}). \tag{5}$$

The ΔH_{subst} values are expected to be positive because the basicity of iodide ion is appreciably weaker than pyridine. And $\Delta H_{\text{lattice}}-\Delta H'_{\text{lattice}}$ values are also expected to be positive, as the $\Delta H_{\text{lattice}}$ values of the ionic crystals of [Co(R,CH_3-dioxH)$_2$(py)$_2$]I are considered to be larger than those of the molecular crystals of [Co(R,CH_3-dioxH)$_2$(py)I]. Hence, it is reasonable that ΔH values are found to be positive as given in Table 2.

Furthermore, judging from the positive ΔH values and with $\Delta G=\Delta H\text{-}T\Delta S<0$ for the occurrence of reaction, large increases in the S values are indispensable in the present reactions. The ΔS values calculated for the present reactions are given in Table 2. Such large increments in the S values, as seen in Table 2, would be brought about by elimination of gaseous pyridine from the solid system. An evaluated ΔS value of the reaction, pyridine(solid)→pyridine(gas) at 431 K was *ca.* 125 J K^{-1} mol^{-1} when C_p (molar heat capacity at constant pressure) was assumed to be 106 J K^{-1} mol^{-1} in the gas phase and 133 J K^{-1} mol^{-1} in the liquid and solid phases.

Kinetics. The reactions (Eq. 1) fitted well the Avrami-Erofeev equation, Eq. 2, wherein n=1; it would be interpreted as that the reactions proceeded one-dimensionally after nucleation had occurred. For comparison, the rate constants, k values, of the reactions are normalized to those at 400 K. These values, as seen in Table 3, increase in the following order of R; $CH_3<C_2H_5<n\text{-}C_3H_7<n\text{-}C_4H_9$. Therefore, it is generally expected that the activation enthalpies ΔH^{*} values, increase in the inverse order of R in the above. In fact, this trend is seen in Table 3. If the ΔH^{*} value were considered to reflect mostly the strength of the Co^{III}-pyridine bonding, the increase in the ΔH^{*} value could be explained as follows: the electron donating alkyl groups behave to increase the electron density on the dioximato moiety, and hence, to decrease the Lewis acidity of the cobalt atom; these resulted in a weakening of the Co^{III}-pyridine bonding. A longer-carbon-chain alkyl group may weaken the Co^{III}- pyridine bonding more extensively.

The activation entropies, ΔS^{*} values, are positive and rather large, as given in Table 3. This fact is in line with the assumption that the reaction follows the S_N1 mechanism, that is, the reaction rate is controlled not by the anation, but by the pyridine dissociation process.[3] The fact that the k values increase in the above order of R also supports the S_N1 reaction mechanism.

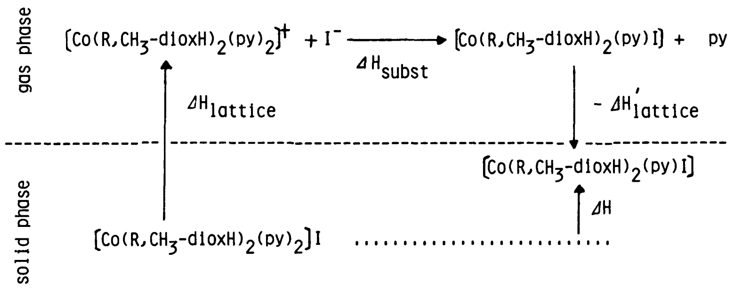

Fig. 4. Thermodynamic cycle proposed for the reaction given in Eq. 1. ΔH_{subst}; energy for substitution reaction in the gas phase, $\Delta H_{\text{lattice}}$ and $\Delta H'_{\text{lattice}}$; lattice energy.

Table 3. Kinetic data of pyridine liberation-anation reactions of the complexes, [Co(R, CH_3-dioxH)$_2$(py)$_2$]I

R	E / kJ mol^{-1}	log (A/s^{-1})	k(400K) / s^{-1}	ΔH^{*}(400K) / kJ mol^{-1}	ΔS^{*}(400K) / J K^{-1} mol^{-1}
CH_3	266± 9	31.0±1.1	(1.78±0.21)×10^{-4}	263± 9	338±21
C_2H_5	232±15	27.7±1.9	(2.04±0.23)×10^{-3}	229±15	275±36
n-C_3H_7	214± 8	27.5±1.1	(3.39±0.30)×10^{-1}	211± 8	271±21
n-C_4H_9	210± 7	27.1±1.0	(4.16±0.40)×10^{-1}	207± 7	263±19

As mentioned above, when the complexes included R groups with longer-carbon-chains, they underwent reaction with smaller ΔH^* values. In order to disclose the contribution of the entropic term to the reactions, the ΔG^* values are calculated by the relation, $\Delta G^* = \Delta H^* - T\Delta S^*$, and are plotted against the ΔH^* values in Fig. 5-A. The relation in Fig. 5-A indicates that the ΔG^* values decrease with decreasing ΔH^* values, *i.e.*, ΔG^* values decrease in the order of R as $CH_3 > C_2H_5 > n\text{-}C_3H_7 > n\text{-}C_4H_9$. This relation indicates that the ΔS^* values are almost definite for the reactions of the series of the complexes examined here. By taking into account the relation, $k = kT/h \exp(-\Delta G^*/RT)$, it is expected that the k values increase in the above order of R. The relation between ΔG^* and ΔH^* values, disclosed above, is in contrast to that known for the thermal, $[Co^{III}(salen)L] \rightarrow [Co^{II}(salen)]$ reactions; in the latter case, the extended alkyl groups on L resulted in the decrease in the ΔG^* values and the increase in the ΔH^* values, indicating that the reaction is dominated by the entropy term.[3] It is demonstrated in Fig. 5-B.

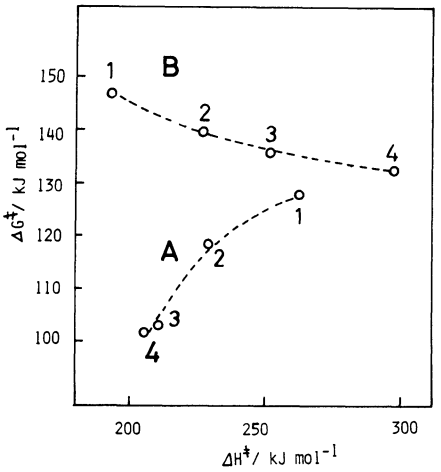

Fig. 5. Relation between ΔG^* and ΔH^* values.
A, $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$: 1, $R=CH_3$; 2, $R=C_2H_5$; 3, $R=n\text{-}C_3H_7$; 4, $R=n\text{-}C_4H_9$.
B, [Co(salen)L]: 1, L=pentanedionato; 2, L=hexanedionato; 3, L=heptanedionato; 4, L=nonanedionato.

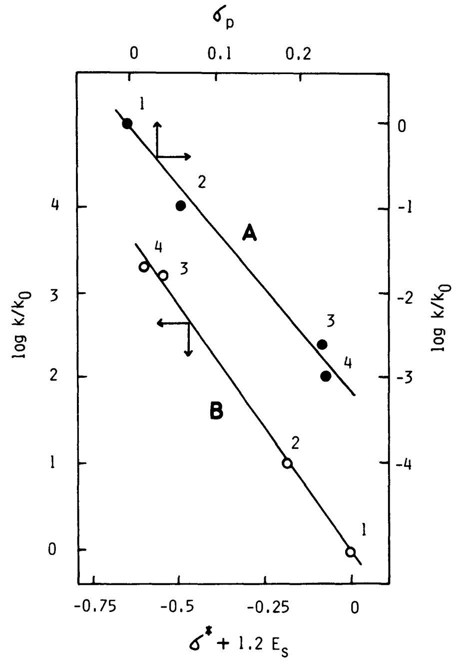

Fig. 6. A; Hammett's plots for pyridine liberation reactions of $Ni[N\text{-}(R\text{-}C_6H_4)salam]_2(py)_2$: 1, R=H; 2, R=*p*-F; 3, R=*p*-Cl; 4, R=*p*-Br.
B; Taft's plots for pyridine liberation-anation reactions of $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$: 1, $R=CH_3$; 2, $R=C_2H_5$; 3, $R=n\text{-}C_3H_7$; 4, $R=n\text{-}C_4H_9$.

For the thermal pyridine liberation reactions of $Ni[N\text{-}(R\text{-}C_6H_4)salam]_2(py)_2{}^*$ (R=H, *p*-F, *p*-Cl and *p*-Br),[9] Hammett's plots of the log k/k_0 (400 K) against σ_p are shown in Fig. 6-A. The linear relation, seen in Fig. 6-A, indicates that the rate constant k is controlled dominantly by the electron-donating inductive effect of the substituent, R. Similar plots were attempted for the present series of the complexes. However, no linear relation was found. An inspection of a stereo model of these complex molecules implies steric interference which might exist beween the extended R groups and the axial pyridine ligands. Evidence for the above type of interference can be obtained by applying the following Taft's relation for the analyses of the reactions:

$$\log k/k_0 = \rho^*\sigma^* + \delta E_s$$
$$= \rho^*\left(\sigma^* + \frac{\delta}{\rho^*}E_s\right). \qquad (6)$$

In Eq. 6, σ^* and E_s are, as have been defined by Taft, polar and steric substituent constants, respectively; ρ^* and δ are definite value with respect to a series of analogous reactions and these are parameters susceptible, respectively, to the polar and steric effects of the substituents. The relation given by Eq. 6 has been observed extensively for the organic reactions; for example, the methanolysis reactions of 1-mentyl esters of a series of aliphatic carboxylic acid, $RCO_2C_{10}H_{19}$, are clearly shown to be affected by both steric and electronic effects of R groups with extended-carbon-chains.[10] The fact that the ΔS^* values are nearly definite for the reactions of the present complexes is considered to support the application of the Taft equation. For, if the ΔS^* values were remarkably differed from each other in the series of reactions, the ρ^* and δ values would vary appreciably with temperature. As Fig. 6-B shows, a good linear relation is observed when log k/k_0 is plotted against $\sigma^* + 1.2\ E_s$; ρ^* and δ are calculated to be -5.7 and -7.0, respectively. This result indicates that a steric effect due to the R groups as well as the electronic one, can contribute to the pyridine liberation reaction. That is, the Co^{III}-pyridine bonding can be weakened both by steric interference between the R and pyridine groups and by the inductive effect due to R. Thus, the substitution of the R groups having longer-carbon-chains into the complexes causes the decrease both in the ΔH^* and ΔG^* values, hence it causes the increase in the k value.[11]

In summary, the $[Co(R,CH_3\text{-dioxH})_2(py)_2]I$ complexes tend to liberate pyridine at lower temperature by including the R groups with longer-carbon-chain; this is in line with the case of the reactions, [Co^III-

(salen)L]→[Co^{II}(salen)]. However, it is noticeable that in the former case, the R groups behave to decrease the activation enthalpy ΔH^{*}, whereas in the latter case, the R groups substituted on L behave to increase activation entropy ΔS^{*}.

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* R,CH_3-dioxH$_2$: CH_3-C(=NOH)-C(=NOH)-R, py: pyridine, *N,N'*-deen: *N,N'*-diethylethylenediamine, salamH: salicylideneamine.

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11) When 2,3-alkanedione dioxime with R=$CH_2CH(CH_3)_2$ was used, only the mono(pyridine) adduct of [Co{$CH_2CH(CH_3)_2$,CH_3-dioxH}$_2$(py)I] was isolated. It is speculated that if the bis(pyridine) adduct were isolated, its pyridine liberation-anation reaction in the solid state would be very fast; the rate constant k(400 K) is evaluated to be 1.7×10^{7} times larger than that of [Co(CH_3,CH_3-dioxH)$_2$(py)$_2$]I.