

KINETICS OF THERMAL DECOMPOSITION OF SUBSTITUTED PYRIDINE ADDUCTS OF *N,N'*-ETHYLENEBIS(SALICYLIDENE-AMINATO)COBALT(II) IN THE SOLID STATE

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ABSTRACT

Kinetic and thermodynamic aspects of the axial base dissociation of solid Co(salen) (X-py) complexes, X = H (1), 3-Me (2), 4-Me (3), 3,4-Me₂ (4), 3,5-Me₂ (5), 3-NH₂ (6), 3-Cl (7), 3-CN (8), 4-CN (9), have been investigated by means of TG-DSC and isothermal weight-loss measurements. These adducts endothermically dissociate the axial base giving rise to the oxygen-active Co(salen) complex. The axial base dissociation reactions fit the contracting disc equation and the kinetic compensation effect is observed for all the adducts excepting Adducts 4-6. For the remaining adducts the kinetic and thermodynamic stabilities of the Co-(X-py) bond are found to increase linearly with increasing Hammett's substitution constants of X except for Adducts 3 and 9. These results are discussed in terms of the σ and π interactions between cobalt(II) and substituted pyridine. Factors dominating the kinetic bond stability are briefly discussed.

INTRODUCTION

We have previously investigated the kinetic and/or thermodynamic features of pyridine dissociation reactions of Ni(*N*-aryl-salam)₂(py)₂ ** [1], Ni(*N*-R-X-salam)₂(py)₂ [2], and RCo(salen)py complexes [3] in the solid state in order to disclose the influence of the chemical properties of the ligands on the kinetic and thermodynamic stabilities of the metal-pyridine bonds. As these ligands are located at the *cis* or *trans* position of the pyridine in the complex molecule, it was then intended to examine the effect

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** The following abbreviations are used in this paper. salen is *N,N'*-ethylenebis(salicylideneaminato) dianion; X-py, substituted pyridine; Me, methyl group; *N*-aryl-salam, *N*-aryl-salicylideneaminato anion; *N*-R-X-salam, *N*-alkyl-substituted-salicylideneaminato anion; R, alkyl group.

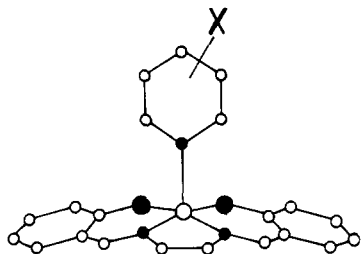


Fig. 1. Co(salen)py molecule.

of the substituents on the pyridine ring itself on the above stabilities. Previous studies have revealed that Hammett's substitution constants or inductive substitution constants are effective parameters to estimate the kinetic and thermodynamic bond stabilities with respect to the metal-pyridine linkage.

This paper describes the thermodynamics and kinetics of substituted pyridine dissociation of [Co(salen) (X-py)] complexes shown in Fig. 1. The results are discussed on the basis of σ and π interactions between Co(II) and the substituted pyridine.

EXPERIMENTAL

Materials

The substituted pyridine adducts examined are listed in Table 1. They were identified by elemental analysis and the magnetic characteristics. Adduct **1** was prepared as previously reported [4]. The other adducts were prepared by the following procedure.

TABLE 1

Analytical and magnetic data

No.	X	Co (%) ^a	C (%) ^a	H (%) ^a	N (%) ^a	$\mu_{\text{eff}}/\mu_{\text{B}}$
1	H	14.66 (14.55)	62.41 (62.38)	4.71 (4.74)	10.19 (10.39)	2.10
2	3-Me	14.20 (14.10)	63.17 (63.16)	4.98 (5.06)	10.09 (10.04)	2.22
3	4-Me	14.21 (14.10)	62.88 (63.16)	4.99 (5.06)	9.91 (10.04)	2.14
4	3,4-Me ₂	13.70 (13.63)	64.05 (63.89)	5.30 (5.36)	9.53 (9.72)	2.18
5	3,5-Me ₂	13.83 (13.63)	63.71 (63.89)	5.35 (5.36)	9.68 (9.72)	2.38
6	3-NH ₂	13.94 (14.05)	60.09 (60.15)	4.75 (4.81)	13.60 (13.36)	2.57
7	3-Cl	13.31 (13.42)	57.43 (57.48)	4.04 (4.13)	9.45 (9.58)	1.98
8	3-CN	13.81 (13.73)	61.68 (61.55)	4.39 (4.23)	12.82 (13.05)	1.69
9	4-CN	14.07 (13.73)	61.42 (61.55)	4.27 (4.23)	12.75 (13.05)	1.98

^a Calculated values (%) are given in parentheses.

Co(salen) (X-py), X = 3-Me (2), 4-Me (3), 3,4-Me₂ (4), 3,5-Me₂ (5)

A solution of Co(salen) (10 mmol) in the substituted pyridine (40 cm³) was refluxed in a nitrogen atmosphere for 12 h. On cooling the solution to room temperature, dark brown crystals separated; these were collected on a filter and washed thoroughly with diethyl ether and then dried in a vacuum desiccator.

Co(salen) (X-py), X = 3-NH₂ (6), 3-Cl (7), 3-CN (8), 4-CN (9)

An ethanol or petroleum ether solution (100 cm³) of the substituted pyridine (25 g) containing Co(salen) (10 mmol) was refluxed in a nitrogen atmosphere for 5 h. The precipitate formed was filtered off while the solution was hot, and then washed thoroughly with warm petroleum ether and dried in a vacuum desiccator.

Measurements

The TG and DSC curves were recorded as previously reported [1]. The kinetic analysis of the axial base dissociation reactions was made on the isothermal weight-loss curves recorded on a Sinku Riko thermal analyzer (Model TGD-3000RH). The heat of dissociation of the axial base and that of sublimation for 3-NH₂-, 3-CN- and 4-CN-py were determined from the DSC peak area measurements [5]. The instrument was calibrated against the heat of transition of potassium nitrate [6].

RESULTS

The elemental analytical data in Table 1 indicate that the reaction of Co(salen) with the substituted pyridines led to the isolation of the adducts with the cobalt-to-base ratio of 1 : 1. Calligaris et al. have reported that the crystal of Adduct 1 consists of monomeric [Co(salen) (py)] molecules in which the cobalt atom has a square pyramidal coordination polyhedron and the apical position is occupied by a pyridine molecule, as shown in Fig. 1 [7]. The other adducts are considered to have the same coordination structure on the basis of their magnetic properties given in Table 1.

The TG and DSC curves of Adduct 1 indicated that it dissociates the axial pyridine molecule endothermally over the 400–450 K range and the corresponding weight loss of 19.2% agrees with the calculated value of 19.6% assuming that one mole of pyridine is eliminated from one mole of the complex. On standing in air, the product took up oxygen as has been reported by Bailes and Calvin [4]. Similarly, the remaining adducts dissociated the axial base endothermally leaving behind the oxygen-active Co(salen). The thermoanalytical data are given in Table 2.

The kinetics of the axial base dissociation were analyzed on the basis of

TABLE 2

Thermoanalytical and kinetic data for the axial ligand dissociation reactions of Co(salen) (X-py) complexes

No.	X	TG weight loss ^a	DSC			Kinetic		
			ΔH_r ^b	ΔH_{sub} ^b	ΔH_{diss} ^b	ΔH_{400}^* ^c	ΔS_{400}^* ^d	$\ln k_{400}$ ^e
1	H	19.24 (19.55)	66.6 ± 0.7	43.7	22.9 ± 0.7	109 ± 4	-46 ± 10	-8.42
2	3-Me	21.87 (22.26)	76.0 ± 0.2	49.3	26.7 ± 0.2	117 ± 6	-28 ± 14	-8.65
3	4-Me	21.81 (22.26)	64.6 ± 0.2	50.7	14.1 ± 0.2	105 ± 3	-53 ± 8	-8.11
4	3,4-Me ₂	24.61 (24.76)	80.4 ± 0.2			125 ± 1	-15 ± 3	-9.62
5	3,5-Me ₂	24.27 (24.76)	79.1 ± 0.3			113 ± 6	-48 ± 15	-9.85
6	3-NH ₂	23.07 (22.44)	88.0 ± 0.4	52.6 ± 1.3	35.4 ± 1.4	112 ± 6	-75 ± 6	-12.90
7	3-Cl	26.39 (25.95)	67.6 ± 0.7			130 ± 2	12 ± 4	-7.91
8	3-CN	24.54 (24.23)	51.1 ± 0.2	42.0 ± 0.1	9.1 ± 0.1	112 ± 10	-30 ± 13	-7.48
9	4-CN	24.23 (24.23)	77.2 ± 0.2	31.5 ± 1.1	45.7 ± 1.1	126 ± 3	5 ± 8	-7.49

^a Calculated values (%) are given in parentheses.

^b ΔH_r , heat of reaction; ΔH_{sub} , heat of sublimation of the X-py ligands; $\Delta H_{diss} = \Delta H_r - \Delta H_{sub}$ (kJ mol⁻¹).

^c Activation enthalpy at 400 K (kJ mol⁻¹).

^d Activation entropy at 400 K (J K⁻¹ mol⁻¹).

^e Rate constant at 400 K (s⁻¹).

the isothermal weight-loss curves. For all the adducts, the dissociation process was found to fit the contracting disc equation well

$$1 - (1 - \alpha)^{1/2} = kt$$

where α is the degree of conversion; k , the rate constant; and t , the time. This is exemplified with the results obtained for Adduct 1 in Fig. 2. Figures

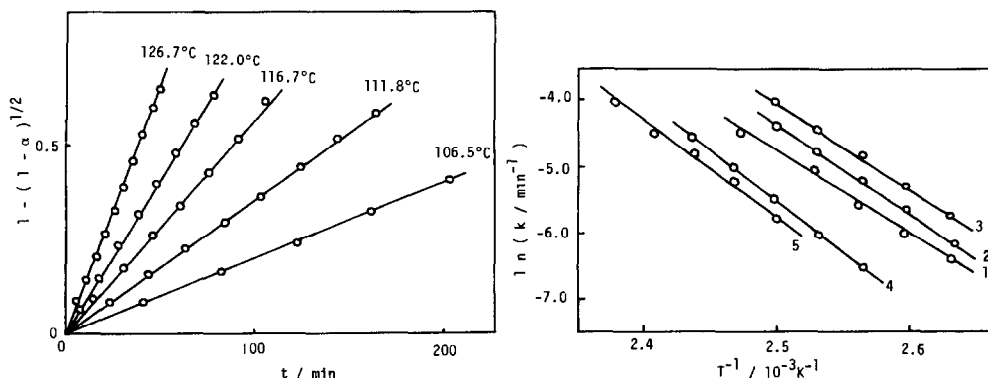


Fig. 2. Contracting disc rate plots for pyridine dissociation reaction of Co(salen)py.

Fig. 3. Arrhenius plots for the axial base dissociation reactions of Adducts 1-5.

3 and 4 show the Arrhenius plots. The activation energy, E_a , and pre-exponential factor, A , are calculated from the slope and the vertical intercept, respectively, of the straight line in Figs. 3 and 4 by means of the least-squares method. These values were then reduced to the activation enthalpy, ΔH^\ddagger , and the activation entropy, ΔS^\ddagger , by using the following equations

$$\Delta H^\ddagger = E_a - RT$$

$$\Delta S^\ddagger = R[\ln(Ah/kT) - 1]$$

where h is the Plank constant; k , the Boltzmann constant; and R , the gas constant. For the sake of comparison of the kinetic stability of Co-N(X-py) bonding, the rate constant at 400 K, k_{400} , was calculated. Kinetic data are collected in Table 2.

DISCUSSION

Kinetic bond stability

The kinetic stability of the Co-N(X-py) bond is expected to vary depending on the nature of the substituents on the pyridine ring. Plots of ΔH^\ddagger values against ΔS^\ddagger values exhibit a linear correlation except for Adducts 4–6 (Fig. 5), implying that the reaction mechanism of the base dissociation reactions of Adducts 4–6 is not the same as that for the remaining adducts.

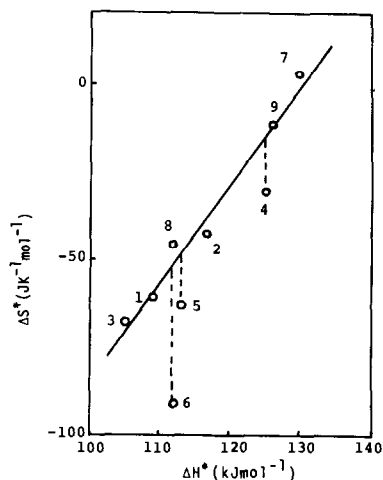
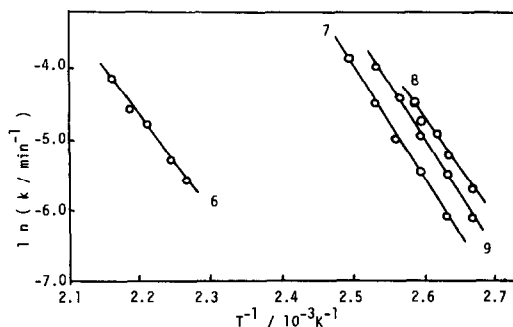
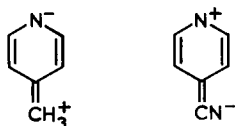


Fig. 4. Arrhenius plots for the axial base dissociation reactions of Adducts 6–9.

Fig. 5. Plots of ΔH^\ddagger vs. ΔS^\ddagger for the axial base dissociation reactions of the adducts.

Therefore, the kinetic data for Adducts 4–6 are left out of the following consideration.

When the logarithmic values of the rate constant at 400 K, $\log k_{400}$, are plotted against Hammett's substitution constants, σ_m and σ_p , a linear correlation is observed, except for Adducts 3 and 9, as shown in Fig. 6. Adduct 3 with 4-Me-py is less stable while Adduct 9 with 4-CN-py is more stable than expected from their σ_p values. Similar observations have been reported in the thermal substituted-pyridine dissociation reactions of $\text{Ag}(\text{X-py})_2\text{NO}_3$ [8] and $\text{Pd}(\text{X-py})_2\text{Cl}_2$ complexes [9]. A linear relationship has been found between $\log k_{400}$ and $\text{p}K_b$ values of X-py for the former complexes and between the ΔH^\ddagger values of the reaction and the $\text{p}K_b$ values for the latter complexes, except for the complexes with *para*-substituted pyridines. Furthermore, it has recently been reported that in the thermal decomposition of $\text{VO}(\text{dibenzoylmethanato})(\text{X-py})$ complexes a linear correlation exists between the $\text{p}K_b$ values and the DSC initial temperature except for *para*-substituted pyridines [10]. These facts suggest that the kinetic stability of metal-substituted pyridine bonds mainly depends on the σ -donating power of the substituted pyridine. Since the bonding consists of σ and π interactions between metal and substituted pyridines, the irregularity observed in the adducts with *para*-substituted pyridines has been interpreted by taking into account the significant contribution of metal–ligand π back-bonding to the bond stability [8–10]. As is indicated by the resonance forms of 4-Me- and 4-CN-py shown below



the *para*-methyl group makes it difficult to accept the metal *d*-electrons while the *para*-cyano group facilitates their acceptance. This explanation appears to be valid in accordance with the irregularity in the present adducts although no data are available on the molecular structure of these adducts, pertinent to consider the π interaction between Co(II) and the substituted pyridine.

As for the nickel(II) complexes [1,2] the substituents on the aryl rings in the equatorial ligands have been found to cause little change in the extent of Ni(II)–py π interaction. The substituents on the pyridine ring, therefore, are considered to exert a more pronounced effect on the metal–py π interaction than those of the equatorial group. These results, however, never signify that the equatorial group is independent of the π interaction between metal and axial ligand: the kinetic study of the NO dissociation reaction of the nitrosylcobalt(III) complexes with “salen” and its derivatives has indicated that the electron-donating group on the aryl ring tends to increase the extent of π interaction between Co(III) and the axial nitrosyl group [11].

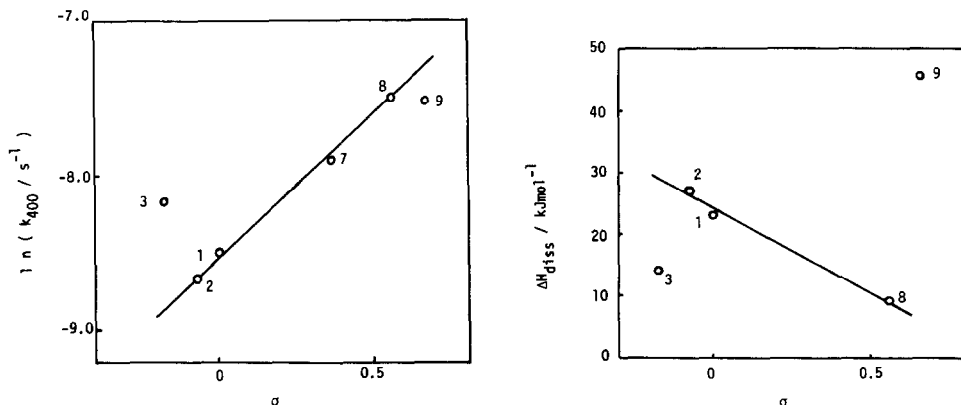
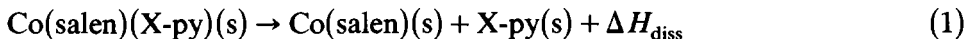


Fig. 6. Plots of Hammett's σ values against $\ln k_{400}$ values for the axial base dissociation reactions of Adducts 1-3 and 7-9.

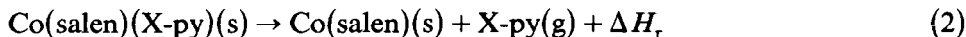
Fig. 7. Plots of Hammett's σ values against ΔH_{diss} values for the axial base dissociation reactions of Adducts 1-3, 8 and 9.

Thermodynamic bond stability

It is convenient to consider the thermodynamic stability of Co(II)-N(X-py) bonding in the solid state on the basis of the assumptive reaction



where (s) means the solid state. As the entropy change accompanied by reaction (1) is considered to be small, ΔH_{diss} can be taken as a measure of thermodynamic bond stability. ΔH_{diss} values are evaluated from the difference between the heat of reaction (reaction (2), ΔH_{r}) and the heat of sublimation of the X-py ligands (reaction (3), ΔH_{sub})



where (g) means the gaseous state.

The ΔH_{diss} values given in Table 2 are plotted against the σ_{m} and σ_{p} values of the substituents on the pyridine ring. Again, a linear correlation is seen in the plots, except for 4-Me and 4-CN-py (Fig. 7). The positive deviation of Adduct 9 and negative one of Adduct 3 from the linear correlation can be explained by the same reason as in the case of the Hammett's plots described above.

Factors dominating the reaction rate

Since the rate constant of a reaction is related to the activation enthalpy

and entropy of the reaction by the following equation

$$\ln k = -\Delta H^\ddagger / RT + \Delta S^\ddagger / R + \ln(kT/h)$$

the magnitude of the rate constant depends on both values. In comparative studies on the solid-state reactions of metal complexes with different metal ions or ligands, the difference in reactivity among the complexes has usually been discussed by using ΔH^\ddagger values as a measure of the reactivity and interpreted on the basis of the nature of the metal ions [12] or ligands [9,11,13]. On the other hand, there are some instances in which the difference in reactivity is not ascribable to the difference in the ΔH^\ddagger values. We have recently reported that in thermal L-dissociation reactions of Co(salen)L complexes (L = 2,4-alkanedionato anion) the activation entropy rather than enthalpy dominates the reactivity of these complexes [14]. As for the present substituted-pyridine dissociation reactions, it was not possible to relate either ΔH^\ddagger or ΔS^\ddagger to the $\ln k_{400}$ values which are found to depend on the electronic property of the substituents; the kinetic character of these reactions is intermediate between those of the two cases described above. Therefore, when the reactivity of solid complexes is examined, the contribution of the activation entropy should not be ignored, although the physical meaning of activation entropy in solid-state reactions is not currently definitive. It seems of interest to investigate whether reaction rates are dominated by either the activation enthalpy or entropy, or by both. Such factors are likely to relate the electronic and steric characters of reacting materials; however, it remains the subject of investigations in the future.

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