THE KINETICS OF THE THERMAL PYRIDINE DISSOCIATION OF PYRIDINE[N,N'-ETHYLENEBIS(SALICYLIDENEAMINATO)]-ALKYLCOBALT(III) IN THE SOLID STATE. KINETIC *TRANS* EFFECT OF ALKYL GROUP

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ABSTRACT

The thermal behavior of RCo(salen)py (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *t*-Bu; salen = N,N'-ethylenebis(salicylideneaminate) dianion; py = pyridine) has been investigated by means of TG, DSC, and isothermal weight-loss measurements. These complexes dissociate 1 mol of pyridine per mole of complex in the temperature range 365–445 K, which is followed by the dissociation of the alkyl group. Kinetic analysis has revealed that the pyridine dissocation reactions fit the contracting disc equation. The electronic nature of the alkyl group has been found to affect the kinetic stability of the Co(III)–alkyl bonding; the more electron-donating group labilizes the Co(III)–py bonding. A linear correlation has been observed between the inductive substitution constants of alkyl groups and the pyridine-dissociation rates at 400 K.

INTRODUCTION

Extensive investigations on the substitution reactions of cobalt(III) and platinum(II) complexes have revealed that certain ligands have a labilizing effect on a ligand coordinated in the *trans* or *cis* position, and such effects are called *trans* and *cis* effects, respectively [1]. Although similar effects are also expected to be observed in ligand-dissociation reactions of transition metal complexes, few papers have appeared in the literature [2]. It was recently reported that the pyridine dissociation rates for solid NiL_2py_2 (L = N-substituted salicylideneaminate anion; py = pyridine) complexes are influenced by the electronic nature of the equatorial ligand, L [3], which can be regarded as an example of the *cis* effect in the dissociation reactions.

In this paper, the *trans* effect of the alkyl group in N,N'-ethylenebis(salicylideneaminato)(pyridine)alkylcobalt(III) complexes (Fig. 1)

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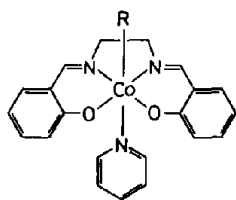
Fig. 1. RCo(salen)py.

has been investigated through the kinetic analysis of pyridine dissociation reactions in the solid state. The complexes are hereinafter abbreviated as RCo(salen)py where R = Me (**1**), Et (**2**), *n*-Pr (**3**), *i*-Pr (**4**), *n*-Bu (**5**), and *i*-Bu (**6**). The *trans* effect of the alkyl group has already been recognized in the substitution reactions of alkylcobalt(III) complexes [4].

EXPERIMENTAL

The pyridine complexes were isolated by the crystallization of the corresponding aqua complexes from a pyridine–methanol (1 : 3) solution and were identified by cobalt analyses and magnetic susceptibility measurements. The aqua complexes were prepared by the method given in the literature [5].

The TG and DSC curves were recorded on a Rigaku Denki 8002 Thermal Analyzer at a heating rate of 5 K min^{-1} in a flowing nitrogen atmosphere. α-Al$_2$O$_3$ was used as reference material. The kinetic analysis of the pyridine dissociation reactions was carried out on the weight-loss curves; these were recorded under isothermal and dynamic (heating rate: 1 K min^{-1}) conditions on a Sinku Riko TGD-3000-RH thermal analyzer in a flowing nitrogen atmosphere. Coats and Redfern's method [6] was employed for the dynamic weight-loss curve analysis. A 15–20-mg aliquot of the sample (particle size: 200–250 mesh) was provided in each run.

RESULTS AND DISCUSSION

The alkylcobalt(III) complexes subjected to the present investigation are shown in Table 1. The complexes were red or reddish brown and showed diamagnetism (χ_g ranged from -0.23 to -0.86×10^{-6} cgs at 298 K) as is expected for cobalt(III) complexes [7].

The TG and DSC curves of the complexes indicated that pyrolysis occurred through three stages. The complexes firstly eliminated the axial pyridine endothermically in the temperature range 365–445 K; the corresponding weight-losses agreed with those calculated by assuming the elimination of 1 mol of pyridine per mole of complex. The products then

TABLE 1

Thermal and kinetic data of the thermal decomposition of RCo(salen)py and Co(salen)py

No.	Complex	Thermal analysis				Kinetic analysis		
		Depyridination		Dealkylation		E_a (kJ mol^{-1})	log A (min^{-1})	$-\log k_{400}$[c]
		Weight-loss[a]	T_m[b]	Weight-loss[a]	T_m[b]			
1	MeCo(salen)py	18.95(18.86)	172	2.17 (3.59)	219	128±1	13.8±0.5	2.85
						128±6[d]	13.9±0.7[d]	
2	EtCo(salen)py	18.41(18.25)	148	4.13 (6.71)	183	84±1	9.4±0.1	1.52
3	n-PrCo(salen)py	17.53(17.68)	109	5.78 (9.63)	206	161±1	20.0±0.1	1.06
4	i-PrCo(salen)py	17.72(17.68)	122	5.83 (9.63)	179	101±1	13.0	0.20
5	n-BuCu(salen)py	17.25(17.14)	92	7.62(12.38)	178	95±1	12.0±0.1	0.45
6	i-BuCo(salen)py	17.19(17.14)	130	7.93(12.38)	148	106±0.1	12.6±0.1	1.17
	Co(salen)py	19.24(19.55)	155			112±4[d]	12.7±0.5[d]	1.93

[a] Calculated values (%) are given in parentheses.
[b] Maximum temperatures (°C) of the DSC peak.
[c] k_{400} = rate constant at 400 K (min^{-1}).
[d] Determined from isothermal weight-loss curves.

dissociated the alkyl group exothermically in the 451 493 K region while the corresponding weight-loss of each complex amounted to only two-thirds of that calculated. Final decomposition occurred in the 473–523 K region. These results are exemplified by the TG and DSC curves of MeCo(salen)py in Fig. 2 and numerical data are given in Table 1. The second step of decomposition has been considered to include the dissociation of the alkyl group as a radical and the subsequent reactions of the radical [8].

The kinetic analysis for the pyridine dissociation reaction carried out on the isothermal weight-loss curves of MeCo(salen)py indicated that the reaction fits the contracting-disc equation

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

where α, k, and t denote the molar fraction of the complex liberated pyridine, the rate constant, and the time, respectively. The rate plots are shown in Fig. 3. Activation energy, E_a, and pre-exponential factor, A, of the reaction were calculated from the slope and intercept of the Arrhenius plot of the rate constants, respectively. The dynamic weight-loss curve analyses carried out using the method of Coats and Redfern also indicate that for all complexes the reactions fit the contracting-disc equation, as shown in Fig. 4. Then the E_a and A values given in Table 1 are calculated by using the relation

$$\ln\left\{2\left[1 - (1 - \alpha)^{1/2}\right]/T^2\right\} = \ln\left[AR/\beta E_a(1 - 2RT/E_a)\right] - E_a/RT$$

where β is the heating rate, R is the gas constant, and T is the temperature. A good agreement is observed in both E_a and A values of MeCo(salen)py which were determined by the above two methods. In order to compare the
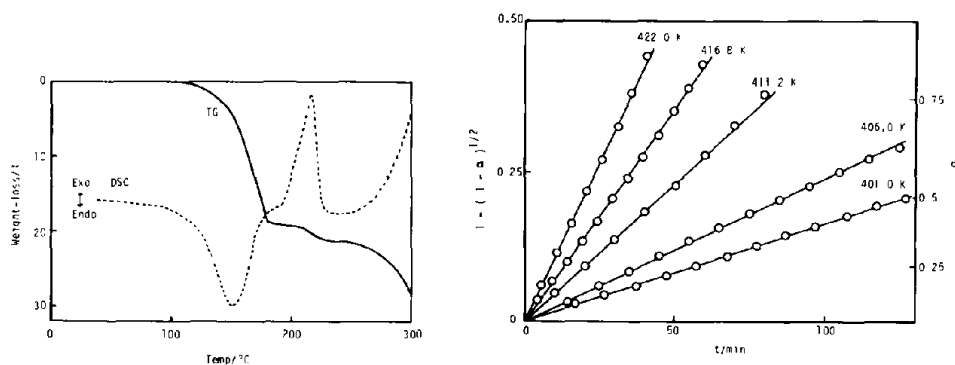

Fig. 2. TG (———) and DSC (- - - - - -) curves of MeCo(salen)py recorded at a heating rate of 5°C min^{-1} in a flowing nitrogen atmosphere.

Fig. 3. Contracting-disc rate plots for the pyridine dissociation reaction of MeCo(salen)py under isothermal conditions.

rate constants they should be normalized [3]. The values at 400 K are taken here; at this temperature all complexes undergo the pyridine dissociation reaction. The logarithmic values of k_{400} given in Table 1 are calculated from the E_a and A values determined under dynamic conditions. It is seen from Table 1 that DSC peak maximum temperatures corresponding to the pyridine dissociation are related to the log k_{400} values.

The log k_{400} values which represent the kinetic stability of the Co(III)–py bonding decrease in the following order of R

Me < Et < i-Bu < n-Pr < n-Bu < i-Pr
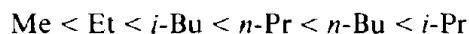
These values correlate linearly with the inductive substitution constants of R [9] except for n-BuCo(salen)py, as shown in Fig. 5. The negative slope of the plots indicates that the more electron donating R-ligand labilizes the bonding between cobalt and pyridine, located at the *trans* position of the R-ligand. As both Co–py and Co–R bondings consist of a σ-covalent bond [10], this result can be interpreted on the basis of the σ-*trans* effect of R [1]. Costa et al. previously reported the rates of substitution reactions in methanol of the alkyl- and arylaqua-1,3-bis(biacetylmonoximeimino)propanatocobalt ion with imidazole, where the kinetic *trans* effect increases in the order [11]: Ph < Me < Et < Pr < i-Pr. They also suggested that these trends might be attributed to increasing electron donating character of aryl or alkyl groups.

The alkylcobalt complexes are depicted formally as having the Co(III)·R⁻ bonding unit [10]. However, their chemical properties have been reported rather to resemble those of Co(II) complexes [11]. This is also confirmed by comparing the kinetic characteristics of pyridine dissociation reactions of RCo^{III}(salen)py and that of Co^{II}(salen)py. The molecular structure of Co(salen)py has been reported to be similar to those of RCo(salen)py, except
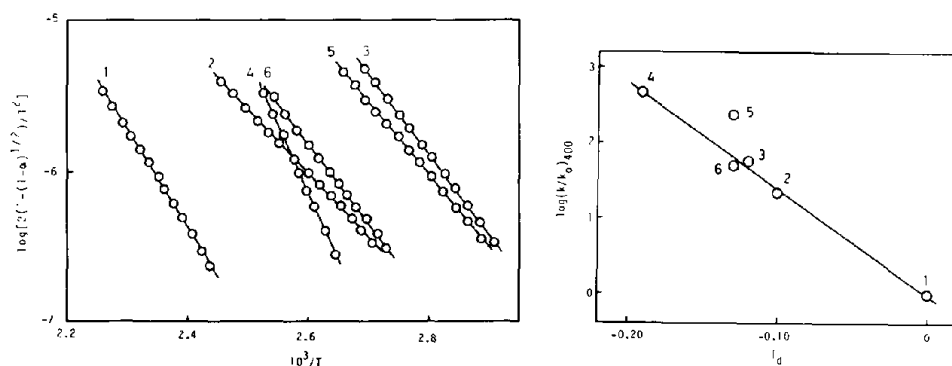

Fig. 4. Rate plots for the pyridine dissociation reactions of RCo(salen)py under dynamic conditions.

Fig. 5. Plots of log(k/k_0) against the inductive substitution constant I_d of alkyl groups. k_0 denotes the rate constant for MeCo(salen)py.
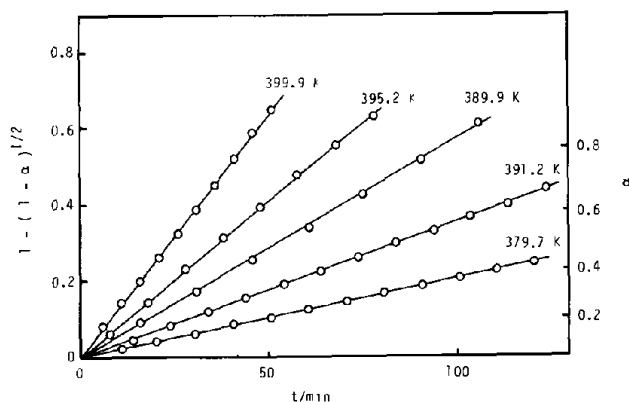
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Fig. 6. Contracting-disc rate plots for the pyridine dissociation reaction of Co(salen)py under isothermal conditions.

for the absence of the axial alkyl ligand [12]. The kinetic analysis of the pyridine dissociation of Co(salen)py indicates that the reaction fits the contracting-disc equation; the kinetic data given in Table 1 are those determined from the isothermal weight-loss measurements (Fig. 6). The log k_{400} value of Co(salen)py is comparable with those of RCo(salen)py complexes.

As for the alkyl dissociation reactions, the DSC peak maximum temperature of the complex with a long chain alkyl group tends to shift to a lower temperature. If the temperature is accepted as a measure of the kinetic stability of Co–R bonding, the alkyl group with a longer chain appears to decrease the kinetic bond stability. Similar trends have been reported for Co(salen)L^2 complexes (L^2 = 2,4-alkanedionate like acetylacetonate anion) that the L^2-dissociation temperatures are lowered with the lengthening of the alkyl chain of the L^2-ligand. This has been ascribed to the steric effects of the L^2-ligands [13].

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