The Thermal Intramolecular Redox Reaction of *N,N'*-Ethylenebis(salicylideneaminato)(2,4-alkanedionato)cobalt(III) in the Solid State**

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The title complexes with the [Co^{III}(salen)L^2] formula, where salen denotes *N,N'*-ethylenebis(salicylideneaminato) dianion and L^2, bidentate 2,4-alkanedionato anions, like the pent, hex, hept, or non anions,† underwent thermally induced, intramolecular one-electron transfer reaction from L^2 to Co(III) in the solid state to give [Co^{II}(salen)] in a stoichiometric amount. The gaseous products evolved on the pyrolysis included 1/2 mol of free 2,4-alkanedione, corresponding to the L^2 of the complexes, per mole of the complexes. The pyrolysis reaction process was described by the contracting-disk equation for all the complexes. The rate constants increased in the following order of L^2: pent<hex<hept<non. The activation enthalpy values were found to increase in the same order. These solid-state reactions are found to be predominantly controlled by the activation entropy.

The thermally induced intramolecular electron-transfer reaction, which occurs in solid transition-metal complexes, is of interest in connection with the physical and chemical properties of such complexes. Many Co(III) complexes seem to have the potential to undergo an electron-transfer reaction from a ligand to Co(III) on heating; however, this reaction tends to be followed by complicated decomposition reactions. Hence, there are very few examples in which the redox reaction can be demonstrated to proceed stoichiometrically. For such complexes as $[Co(NH_3)_6]X_3$ ($X=Cl^-$, Br^-, I^-), $K_3[Co(C_2O_4)_3]$, and *trans*-$[Co(CH_3NH_2)_2(phbgH)_2]Cl_3$,† it has been revealed by the thermoanalytical technique that they undergo a thermally induced electron-transfer reaction from the NH_3, X, or phbgH ligands to the central Co(III) ion.[1] For the thermal dissociation of NO or O_2 from the nitrosyl or dioxygen complexes with a unitary formula, Co(III)-NO^-, Co(III)-O_2^-, or Co(III)-O_2^{2-}-Co(III), it was considered that the electron-transfer occurred from these ligands to Co(III).[2]

Podder and Biswas first prepared the series of complexes with the [Co^{III}(salen)L^2](L^2=2,4-alkanedionato) formula.[3] Subsequent investigations provided the extended series of analogous Co(III) complexes.[4] The crystal X-ray diffraction analysis of [Co^{III}(salen)(pent)]·$0.7H_2O$† has elucidated its octahedral structure, in which pent is coordinated as a bidentate ligand at the cis-position, and salen, as a tetradentate one at the remaining four positions.[5] In the present paper, the solid [Co^{III}(salen)L^2] complexes are shown to undergo the thermally induced, intramolecular one-electron transfer reaction of L^2→Co(III), affording oxygen-active crystals of [Co^{II}(salen)] complex in a stoichiometric amount. Moreover, the kinetic analyses will disclose that the reaction rate is apparently dominated by the factor included in the activation entropy term.

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† The following abbreviations are used: pent, 2,4-pentanedionato; hex, 2,4-hexanedionato; hept, 2,4-heptanedionato; non, 2,4-nonanedionato anions; phbgH, phenylbiguanide; and salam, salicylideneaminato anion.

Experimental

Preparation of Complexes. The 2,4-pentanedione ligand was commercially available. The other 2,4-alkanediones were synthesized according to the literature.[6] The series of [Co^{III}(salen)L^2] complexes, including newly prepared ones with L^2=hept and non, were prepared as follows: [Co^{II}(salen)], obtained by following the literature method,[7] was heated with the appropriate 2,4-alkanedione in a water-acetone (2 : 3) solution on a steam bath for a few minutes. When the solution was cooled, it separated crystals; these were purified by recrystallization from chloroform. The crystals thus obtained were anhydrous; this was confirmed by thermal and elemental analyses. The crystals were hygroscopic in ordinary air and showed diamagnetism at room temperature.

Elemental analysis for [Co(salen)L^2]. Found, (Calcd for anhydride). For L^2=pent: C, 59.10 (59.43); H, 5.02 (4.95); N, 6.52 (6.60); Co, 13.80% (13.90%). For L^2=hex: C, 60.22 (60.28); H, 5.16 (5.29); N, 6.38 (6.40); Co, 13.38% (13.46%). For L^2=hept: C, 60.88 (61.06); H, 5.53 (5.57); N, 6.10 (6.19); Co, 12.81% (13.04%). For L^2=non: C, 62.29 (62.50); H, 6.08 (6.08); N, 5.89 (5.83); Co, 12.25% (12.28%).

The ^{1}H-NMR spectral investigation showed that the complex with L^2=pent had a "cis-β" coordination,[8] δ/ppm values of -CH=N- in the $CDCl_3$ solution: 7.80, 7.57. As for the complexes with L^2=hex, hept and non, three peaks were observed for -CH=N- in the $CDCL_3$ solution; δ/ppm: 7.82, 7.59, and 7.55 for each complex, and the δ values were not different among the three complexes. This observation suggested the two geometrical isomers, such as cis-β_1 and cis-β_2, were present.

Measurements. The TG and DTA curves were recorded in a flowing nitrogen atmosphere at a heating rate of 10 °C/min on a Rigaku Denki thermal analyzer, Model 8002. The kinetic analysis under dynamic conditions was carried out on the TG curves recorded by the use of a Sinku Riko TGD-3000-RH apparatus at a heating rate of 1 °C/min. The particle size of the samples provided for the measurements was under 200 mesh.

The powder X-ray diffractions were recorded on a Rigaku Denki Geigerflex diffractometer, using Co $K\alpha$ radiation and an iron filter.

Pyrolysis gas chromatographic (PGC) measurements[9] were made under the conditions cited in the footnote of Table 1. The calibration curves were drawn by means of the direct injection of known amounts of an appropriate, purified 2,4-alkanedione into the separation column of the

TABLE 1. THERMAL PROPERTIES OF [Co^{III}(salen)L^2]

L^2	Reaction temp/°C[a)]	Weight-loss/% Found	Weight-loss/% Calcd	Evolved HL^2 mol/mol[b)]
pent	216	23.4	23.3	0.47
hex	208	25.3	25.8	0.49
hept	204	27.8	28.1	0.50
non	203	31.7	32.3	0.50

a) Indicated the temperature at which the weight-loss amounted to one-half of the total weight-loss, *i.e.*, $\alpha=1/2$. b) PGC conditions: pyrolysis temperature, 220°C; column packing, DEGA(diethylene glycol adipate polyester); column temperature, 190°C.

instrument; the peak area was recorded on an integrator.

Results

Pyrolysis. The TG-DTA curves for the [Co^{III}(salen)L^2] complexes are shown in Fig. 1. The complexes undergo an endothermic change in the 170—230 °C range, the decrease in the weight corresponding to the elimination of one mol of L^2 per mole of the complexes. In the case of [Co^{III}(salen)(pent)], the elementary analytical results of the solid, pyrolysis product agreed with the results calculated for [Co(salen)]: Found, (Calcd): C, 58.62 (59.08); H, 4.21 (4.31); N, 8.30 (8.62); Co, 18.07% (18.12%). The effective magnetic moment μ_{eff}= 2.51 μ_B (300 K), of the product was consistent with the value, μ_{eff}=2.51 μ_B (296 K), previously reported for the authentic [Co^{II}(salen)];[10] it indicates that one unpaired electron was in the complex molecule. Moreover, the powder X-ray diffraction pattern for the resultant product agreed with that of authentic [Co^{II}(salen)], as is shown in Fig. 2. Similarly, the pyrolyses of the complexes with L^2=hex, hept, and non left behind a product that could be shown to be [Co^{II}(salen)] from the elementary analytical results and from the measurements of the magnetism and the X-ray diffraction.

The PGC analytical results clearly indicated that the gaseous products evolved by the pyrolysis included 1/2 mol of the corresponding free HL^2 per mole of the starting [Co(salen)L^2]. The data are given in Table 1. The production of free HL^2 was also indicated by the ^{1}H-NMR spectra in the DMSO-d_6 solution in which the gaseous products were trapped. In addition, when L^2=pent, the NMR spectral inspection indicated that the gaseous products included indefinite amounts of acetone, methanol and ethanol, besides the principal amount of Hpent.

From the above facts, the thermal reaction can be described as follows:

$$[Co^{III}(salen)L^2] \longrightarrow [Co^{II}(salen)] + 1/2\,HL^2 + X. \quad (1)$$

In Eq. 1, X represents a mixture of such volatile compounds as have been cited above; the further identification of X has not been undertaken here.

Kinetic Analysis. The kinetic analysis was carried out in order to ascertain the kinetic character of the reaction. As has been mentioned, the ^{1}H-NMR spectra suggested that the complexes with L^2=hex,

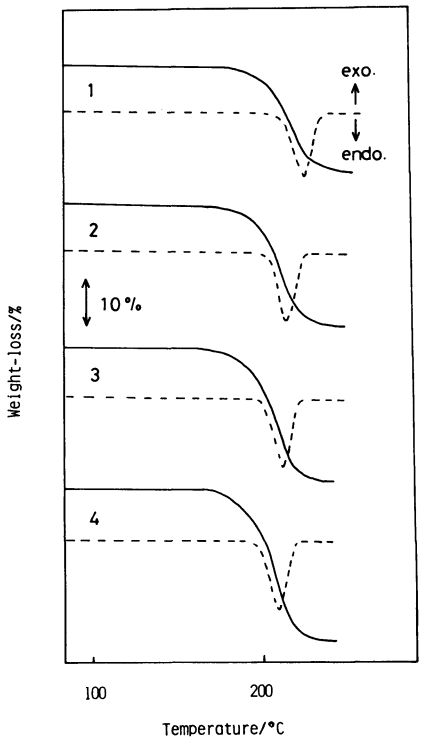

Fig. 1. TG (——) and DTA (----) curves of [Co^{III}(salen)L^2].
1: L^2=pent, 2: L^2=hex, 3: L^2=hept, 4: L^2=non. No response appeared blow 100°C in the TG and DTA curves.

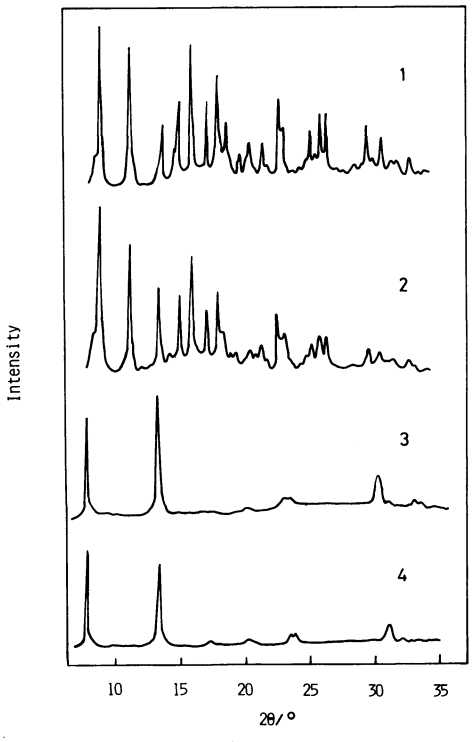

Fig. 2. Powder X-ray diffractograms.
1: [Co^{III}(salen)(pent)]·0.7H_2O, 2: [Co^{III}(salen)(pent)], 3: [Co^{II}(salen)] obtained by the pyrolysis of [Co^{III}(salen)(pent)], 4: authentic [Co^{II}(salen)]; oxygen-active form crystal.

hept, and non in the solution existed in two isomeric forms. However, the TG and DTA curves showed only one-stage changes. Hence, it was assumed that these isomers were thermally indistinguishable in the solid state, if they were present there at all. Then, the rate plots under non-isothermal conditions were obtained by the use of Eq. 2, according to the method developed by Coats and Redfern:[11]

$$\log\{[1-(1-\alpha)^{1-n}]/T^2\} = \log\frac{AR(1-n)}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT}. \quad (2)$$

In Eq. 2, E is the activation energy; A, the pre-exponential factor; α, the molar fraction of [Co^{II}-(salen)]; T, the absolute temperature; R, the gas constant; a, the heating rate. Since, as is shown in Fig. 3, the rate plot of the reaction for [Co^{III}(salen)(pent)] under isothermal conditions was found to fit the contracting-disk equation, $1-(1-\alpha)^{1/2}=kt$ (k, the rate constant; t, the reaction time), n in Eq. 2 is replaced with a value of 1/2. Then, the rate plot, *i.e.*, the $\log\{[1-(1-\alpha)^{1/2}]/T^2\}$ *vs.* $1/T$ plot, gives a straight line, as is shown in Fig. 4. These facts indicate that the reaction fits the contracting-disk equation well for all the complexes investigated. The E and A values were calculated from, respectively, the slope and the intercept of these straight lines. For the sake of comparison, it is desirable to normalize the rate constants to those at a definite temperature. Therefore, the rate constants at 460 K were calculated from the Arrhenius equation, $k=A\exp(-E/RT)$, by using the above E and A values. The activation enthalpy $\Delta H^{\ddagger}$ value was calculated from the $\Delta H^{\ddagger}=E-RT$ relation; while the activation entropy $\Delta S^{\ddagger}$ value was obtained from Eq. 3, assuming the transmission coefficient κ to be 1;

$$\Delta S^{\ddagger} = R[\ln(Ah/\kappa kT) - 1]. \quad (3)$$

In Eq. 3, k is the Boltzman constant, and h, the Planck constant. The kinetic characteristics are tabulated in Table 2.

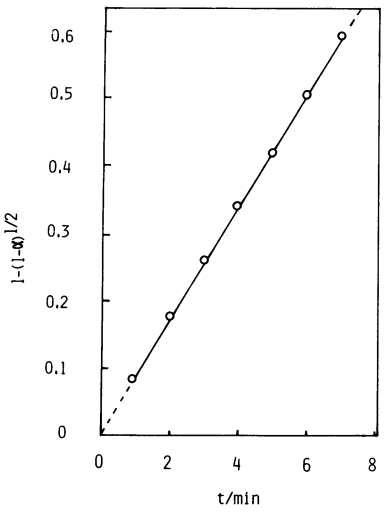

Fig. 3. Rate plots for thermal reaction of [Co^{III}-(salen)(pent)] under isothermal conditions. α; 0.17—0.84.

Discussion

It was shown by the mass spectrometric investigation that, upon pyrolysis, [Co^{III}(pent)$_3$] evolved gaseous products, including principally acetone and CO_2;[12] the redox process of the reaction was not elucidated, however. On the pyrolysis of the [Co^{III}(salen)L^2] complexes, the thermally induced one-electron transfer reaction, L$^2\rightarrow$Co(III), obviously occurred, producing [Co^{II}(salen)] and HL^2 in stoichiometric amounts, as is represented by Eq. 1. As may be seen in Fig. 2, the powder X-ray diffractogram of the anhydrous crystal of [Co^{III}(salen)(pent)], which was prepared here and subjected to pyrolysis, is almost entirely consistent with the diffractogram of the 0.7 hydrate crystal, for which crystal-structure analysis has been performed.[5] The other anhydrous crystals of the complexes investigated also showed well-defined diffractograms, although their crystal systems were not determined. For all the [Co^{III}(salen)L^2] complexes, the pyrolysis left behind [Co^{II}(salen)], which showed a diffraction pattern agreeing with that of authentic [Co^{II}(salen)]. Hence, it can be said that the thermal reaction described by Eq. 1 proceeds accompanied by a crystal-structure change in the pair of [Co^{II}(salen)] and respective [Co^{III}(salen)L^2].

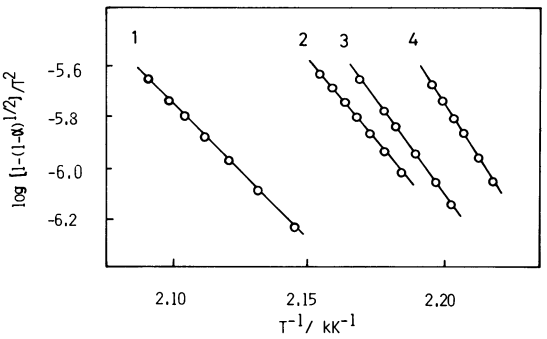

Fig. 4. Rate plots for thermal reactions of [Co^{III}-(salen)L^2] under non-isothermal conditions. 1: L^2=pent, 2: L^2=hex, 3: L^2=hept, 4: L^2=non.

Table 2. Kinetic data of thermal reactions of [Co^{III}(salen)L^2]

L^2	E/kJ mol^{-1}	log(A/s^{-1})	k(460 K)/s^{-1}	$\Delta H^{\ddagger}$(460 K)/kJ mol^{-1}	$\Delta S^{\ddagger}$(460 K)/J K^{-1} mol^{-1}
pent	197±3	18.7±0.5	(2.00±0.72)×10^{-4}	193±3	101±9
hex	231±6	23.4±0.6	(1.38±0.27)×10^{-3}	227±6	190±11
hept	256±9	26.6±0.9	(3.09±0.92)×10^{-3}	252±9	252±17
non	302±11	32.2±1.4	(7.75±2.45)×10^{-3}	298±11	359±26

E, Activation energy; A, pre-exponential factor; k, rate constant; $\Delta H^{\ddagger}$, activation enthalpy; $\Delta S^{\ddagger}$, activation entropy.

The volatile pyrolytic products consisting of HL^2 and other compounds are considered to diffuse through the system as rapidly as that the pyrolytic reaction can be described by only one equation, *i.e.*, the contraction-disk equation, over the range of $\alpha=0.17—0.84$. In such cases as the thermal pyridine dissociation of $Ni[N\text{-}(p\text{-}CH_3\text{-}C_6H_4)salam]_2(py)_2$[7], the reaction proceeds, following the contracting-disk equation in the earlier stage of the reaction, $\alpha=0—0.35$, and according to Jandar's equation in the later stage, $\alpha=0.35—0.75$. This later stage of the reaction was interpreted as showing that the diffusion of the liberated pyridine was slow enough to be observed.[13]

The production of HL^2 can be explained as follows. The thermally induced, homolytic fission of the L^2-Co(III) bond causes a concomitant $L^2\rightarrow$Co(III) one-electron transfer to form the $\cdot L^2$ radical; this derives a hydrogen atom from another $\cdot L^2$ radical to produce HL^2; the dehydrogenated $\cdot L^2$ radical decomposes into lower molecular compounds; these are represented by X in Eq. 1. It is noteworthy that HL^2 was produced quantitatively through such a reaction as occurs in the solid phase. The crystals of the [Co(salen)(pent)]$\cdot 0.7H_2O$ complex belong to the $P2_12_12_1$ space group, suggesting that, in these crystals, two complex molecules are packed as if they were a pair. In the anhydrous crystals, the molecular packing is considered not to be remarkably changed, as is indicated by the powder X-ray diffractograms shown in Fig. 2. Therefore, it may be speculated that this molecular arrangement, forming a pair as above, causes the reaction to proceed stoichiometrically, yielding one mole of Hpent from two moles of [Co(salen)(pent)]. Although the crystal structures for the other complexes have not yet been elucidated, a crystal structure analogous to that of [Co(salen)(pent)] might be suggested from their stoichiometric formation of HL^2.

As may be seen from the above discussion, the kinetic data apparently correspond to the change depicted by Eq. 4;

$$[Co^{III}(salen)L^2]\ (crystal)\rightarrow[Co^{II}(salen)]\ (crystal). \quad (4)$$

In Eq. 4 three processes are involved; i) the bond cleavage of L^2-Co(III), which occurs with a concomitant $L^2\rightarrow$Co(III) electron-transfer, ii) the rearrangement in the coordination geometry from octahedron to square-plane, and iii) the change in the crystal packing from that of $[Co^{III}(salen)L^2]$ to that of $[Co^{II}$-(salen)]. In the following argument, the effect on the kinetic data arising from the difference in the crystal packing of the starting complexes is assumed to be negligible among the complexes of the present series.

Generally speaking, the k value in most reactions decreases as the $\Delta H^{\neq}$ value increases. In the present complexes, the L^2-Co(III) bond can be expected to be more strengthened when the alkyl group substituted on L^2 has a longer chain; the electron-donating property (I-effect) of the alkyl group acts to increase the electron density on the O-atom in L^2 and hence, to strengthen the L^2- Co(III) coordination bond. Therefore, the complex with a longer chain alkyl group on L^2 can be expected to have larger $\Delta H^{\neq}$ values and smaller k values. Actually, however, the reaction

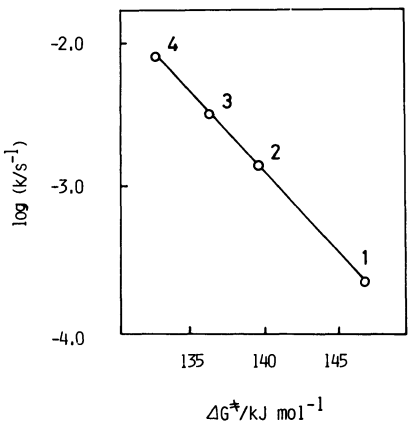

Fig. 5. Relation between log k and $\Delta G^{\neq}$ values at $T=460$ K.
1: L^2=pent, 2: L^2=hex, 3: L^2=hept, 4: L^2=non.

examined here did not occur along these lines. That is, whereas the $\Delta H^{\neq}$ value increased in the order of L^2, pent<hex<hept<non, as predicted, the k value increased in the same order; this is numerically demonstrated in Table 2. This finding led us to consider that the activation entropy might involve a factor favoring the occurrence of these solid-state reactions. The $\Delta S^{\neq}$ value calculated in the case of a complex with L^2=non is *ca.* 3.5 times larger than that with L^2=pent. Therefore, for the complex with L^2=non, the $\Delta G^{\neq}(=\Delta H^{\neq}-T\Delta S^{\neq})$ value comes to be smallest and the k value, largest, among the complexes investigated; this relation between the $\Delta G^{\neq}$ value and the nature of L^2 is shown in Fig. 5.

As Table 2 shows, the $\Delta S^{\neq}$ value of the reaction is positive and rather large. This fact is not contrary to the assumption that the reaction rate is predominantly determined not by the electron-transfer, but by the L^2-Co(III) bond-cleavage reactions. In the transient structure, if the electrons participating in the L^2-Co(III) bonding were withdrawn toward the Co atom, this structure might have a lower entropy than usual. On the other hand, if the L^2-Co(III) bond were relaxed, this structure might have an increased entropy due to the increased freedom of L^2. By accepting the latter transient structure, it could be understood that the $\Delta S^{\neq}$ value of the reaction for the complex with L^2=non is larger than that for the complex with L^2=pent. In conclusion, L^2 ligands with longer alkyl chains cause the solid-state reaction of the complexes examined here to occur more easily through the entropic factor.

The crystalline $[Co^{II}(salen)]$ complex obtained by the pyrolysis took up oxygen in a dry air or an oxygen atmosphere at room temperature. The O_2-adduct liberated oxygen endothermally at *ca.* 65 °C, thus decreasing the weight by 4.8%; this indicated that the composition of the adduct was $[Co(salen)]_2\cdot O_2$. There have appeared in the literatures two crystalline forms of the $[Co^{II}(salen)]$ complex; one is active, and the other, inactive, toward oxygen-uptake;[7] the active form takes up oxygen reversibly in a molar ratio of Co(II) : O_2= 2 : 1. It has also been reported that the pyrolysis of the solid $[Co^{II}(salen)(py)]$ or $[Co^{II}$-

(salen)($CHCl_3$)] leaves behind the oxygen-active complex of [Co^{II}(salen)].[14]

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