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Thermoanalytical Study of Dioxygencobalt(III) Complexes with *N,N'*-Ethylenebis(salicylideneaminate) and Its Derivatives

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The oxygen-dissociation reactions of $[Co(3\text{-}X\text{-}salen)]_2O_2$, where 3-X-salen is *N,N'*-ethylenebis(3-substituted salicylideneaminate) dianion, X=H (**1**), OCH_3 (**2**), OC_2H_5 (**3**), NO_2 (**4**), have been studied by means of a thermoanalytical technique. The heat of the reaction, determined by DTA, ranges from 88 (**4**) to 120 (**2**) kJ mol^{-1}; the electron-releasing substituents tend to stabilize the Co–O_2 bonding. The O_2-dissociation process is best described by the first-order equation and the activation enthalpies range from 117 (**4**) to 145 (**2**) kJ mol^{-1} and the electron-releasing substituents increase the activation enthalpy. A kinetic compensation effect was observed, except for **3**, which is the most stable of these complexes due to its small activation entropic value.

We previously reported the kinetics of thermal decomposition of cobalt(III) complexes which is accompanied by concomitant redox reactions between the ligand and the cobalt(III) ion.[1—3] Through this study we found that the activation enthalpy of the redox reaction can be related to the reducing power of the reductant, and that the activation entropy plays an important role in determining the thermal stability of the complexes. In order to obtain additional examples we studied the kinetics of the thermal decomposition of $[Co(3\text{-}X\text{-}salen)]_2O_2$, where 3-X-salen denotes *N,N'*-ethylenebis(3-substituted salicylideneaminate) dianion and X=H (**1**), OCH_3 (**2**), OC_2H_5 (**3**), NO_2 (**4**) in the solid state. The formation of the dioxygen complex by the reaction of oxygen with solid Co(salen) was first reported by Tsumaki;[4] and the kinetics and thermodynamics of the oxygenation reactions of the present complexes were studied by Calvin and co-workers.[5,6]

Experimental

The dioxygen complexes were prepared by the reaction of oxygen with Co(3-X-salen), which is prepared from either [Co(3-X-salen)py] (**1**) or $[Co(3\text{-}X\text{-}salen)H_2O]$ (**2**—**4**) upon heating. These pyridine and aqua complexes were prepared by a method described in the literature,[7] and were identified by cobalt analyses and the weight loss due to the base liberation upon heating (Table 1).

The TG-DTA curves of the O_2-liberation reaction were recorded in a flowing nitrogen atmosphere on a Rigaku Denki Thermoflex, α-alumina being used as a reference. The dioxygen complexes were prepared just before the measurement: 15—20 mg of the mono base adduct (particle size>200 mesh) was placed in a sample pan; it was then heated in nitrogen atmosphere to complete the liberation of the base. The sample was then cooled to room temperature and oxygen gas was flowed over the sample to complete the oxygenation reaction. Completion of oxygenation was checked by monitoring the weight gain due to oxygen up-take. The heating rate were 1 K min^{-1} for the measurement of the dynamic weight-loss (DWL) curves which were utilized for the kinetic analysis of the reaction and 5 K min^{-1} for the DTA peak-area measurements. The instrument was calibrated against the heat of transition of potassium nitrate. The isothermal weight-loss (IWL) curves were recorded on a Sinku Riko TGD 3000-RH in a flowing nitrogen atmosphere.

Results and Discussion

All Co(3-X-salen) complexes, except for Co(3-NO_2-salen), absorbed at room temperature a stoichiometric amount of oxygen, forming μ-peroxobiscobalt(III) complexes. The Co(3-NO_2-salen) complex did not absorb more than 70% of the calculated value for complete oxygenation. The TG-DTA curves of the present complexes are shown in Fig. 1. These dioxygen complexes endothermically liberated absorbed O_2 over the 300—400 K range to give rise to their parent complexes (Eq. 1),

Table 1. Analytical and Thermoanalytical Data of Co(3-X-salen)Y and $[Co(3\text{-}X\text{-}salen)]_2O_2$ Complexes[a)]

X	Y	Co/%	Weight-loss/%[b)]	Weight-gain/%[c)]	$\Delta H^{\ne}_{335}$	$\Delta S^{\ne}_{335}$	$-\ln k_{335}$	ΔH_r
		Found(Calcd)	Found(Calcd)	Found(Calcd)	kJ mol^{-1}	J K^{-1} mol^{-1}	s^{-1}	kJ mol^{-1}
H	py	14.66(14.55)	19.51(19.55)	4.52(4.92)	123±3	88±1	4.15±0.97	96±5
OCH_3	H_2O	14.39(14.61)	4.46(4.46)	4.08(4.15)	145±6	152±3	4.25±1.75	120±6
OC_2H_5	H_2O	13.72(13.66)	4.16(4.18)	3.85(3.87)	140±4[d)]	119±12[d)]	6.36±1.95[d)]	104±5
					138±7	108±0	7.14±2.5	
NO_2	H_2O	13.59(13.60)	4.11(4.15)	2.76(3.85)	117±4	75±1	3.50±1.4	88±4

a) Unless otherwise noted, kinetic data were determined from DWL curves. b) Weight-loss due to base liberation reaction. c) Weight-gain due to oxygen up-take. d) Determined from the IWL curves.

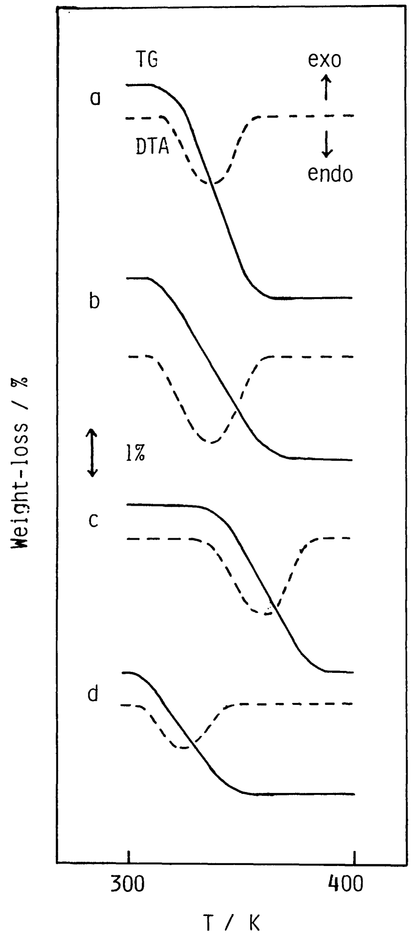

Fig. 1. TG-DTA curves for $[Co(3\text{-}X\text{-}salen)]_2O_2$. a: X=H (**1**); b: $X=OCH_3$ (**2**); c: $X=OC_2H_5$ (**3**); d: $X=NO_2$ (**4**).

$$[Co(3\text{-}X\text{-}salen)]_2O_2\,(s) \longrightarrow 2Co(3\text{-}X\text{-}salen)(s) + O_2\,(g). \quad (1)$$

Since in the dioxygen complexes two Co(3-X-salen) moieties are bridged through the peroxo anion and the oxidation state of cobalt ion is III, the reaction is considered to be accompanied by a concomitant reduction of Co(III) to Co(II) by the peroxo anion. The heats of reaction determined by the DTA method in a nitrogen atmosphere are given in Table 1. These values range from 88 to 120 kJ mol^{-1} and decrease in the order of X: $OCH_3 > OC_2H_5 > H > NO_2$. These data, however, disagree with the heat of the reverse reaction of **1**, reported by Hughes et al;[6] they reported the heat of oxygenation of Co(3-X-salen), X=H, OCH_3, and OC_2H_5 to be around -80 kJ mol^{-1}, regardless of the sort of X from calorimetric and equilibrium studies of Reaction 1. The origin of this difference in the heat of reaction cannot be readily assessed.

When the difference in the sublimation energies between a pair of dioxygen and parent complexes is not very large for the different X, the heat of reaction of solid-state oxygenation or deoxygenation can be taken as a measure of the strength of the cobalt–dioxygen bond. The effects of the subsituents on the aryl ring regarding bonding can be considered from steric and electronic standpoints separately. Although the structural data of the dioxygen complexes, indispensable for estimating the steric effect, are not available, it is considered that the substituents on the 3-position of the aryl ring do not have a significant intramolecular steric interaction with the coordinated oxygen molecule from molecular modeling. As far as the electronic effects are concerned, our data indicate that the electron-releasing groups strengthen the bonding, while the data of Hughes et al. imply no influence of the substituents. Since other thermodynamic data concerning the formation of μ-peroxocobalt(III) complexes are not available, it is impossible to draw any conclusion as to the influence of the substituents on the bonding.

There have been several studies on the thermodynamics of the formation of hyperoxocobalt(III) complexes in solution, from which we can depict the influence of the substituents on the cobalt–dioxygen bonding. Chen et al.[8] have reported thermodynamic data concerning the binding between dioxygen and cobalt(II) complexes in toluene,

$$Co(p\text{-}X\text{-}bzacen)(py) + O_2 \longrightarrow Co(p\text{-}X\text{-}bzacen)(py)O_2, \quad (2)$$

where *p*-X-bzacen denotes *N,N′*-ethylenebis(2-*p*-X-benzoyl-1-methylethylideneaminate) dianion; py= pyridine; and X=H, OCH_3, CH_3, Cl, and Br. The enthalpies of Reaction 2 fall within a narrow range, -72.4 to -67.8 kJ mol^{-1}, while both electron-releasing and -withdrawing substituents tend to stabilize the Co(III)-O_2^- bonding. Furthermore, Walker et al.[9] have reported on thermodynamic data concerning the reaction in dichloromethane,

$$Co(p\text{-}X\text{-}tpp)(py) + O_2 \longrightarrow Co(p\text{-}X\text{-}tpp)(py)O_2, \quad (3)$$

where *p*-X-tpp denotes *p*-substituted *meso*-tetraphenylporphyrin dianion and X $=OCH_3$, H, F, Cl and CN. The enthalpies of Reaction 3 (-39.9 to -35.1 kJ mol^{-1}) are almost invariable with a change in the substituents on the phenyl ring. Both data seem to support the results of Hughes et al. that the electronic effects of the substituents are not a major factor determining the stability of Co-O_2 bonding. On the other hand, Carter et al.[10] have studied the influence of the organic base of Reaction 2 on the oxygen uptake constants, and found a linear correlation between the constants and the $E_{1/2}$ values for Co(II)→Co(III) of the Co(bzacen)(base) complexes. MacLendon and Martell[11] have found a good linear free-energy relation between the dioxygen uptake constants and the protonic basicity of the ligands in the following reaction:

$$2[CoL(H_2O)_2]^{3+} + O_2 \longrightarrow [Co_2(O_2, OH)L_2]^{3+}, \quad (4)$$

where L denotes bidentate to quadridentate amines. A complex with the stronger base forms the stabler complexes. Jones et al.[12] have interpreted this fact as follows: Since these systems involve a charge transfer from cobalt to dioxygen upon coordination, the stronger is the base strength of the ligands, the greater is the electron density on cobalt, the greater is the electron transfer from cobalt to dioxygen, and the stabler is the dioxygen complex. Different from Chen and Walker, these facts suggest that the substituent has a potential to affect the Co–O_2 bonding; the present results are in line with this interpretation as the electron-releasing substituent increases the Lewis basicity of the ligand. The electronic nature of the substituent on the aryl ring has been shown to affect metal–ligand bonding through the thermal decomposition of bis(*N*-methyl-5-substituted salicylideneaminato)bis(pyridine)nickel(II) in the solid state.[13]

Kinetics. The kinetic analysis of the deoxygenation reaction was carried out in order to evaluate the kinetic stability of the cobalt–dioxygen bond in the present complexes. The IWL curves of Complex **3** recorded over the range of 330 to 339 K were utilized to determine the reaction mechanism. As shown in Fig. 2, the reaction fits the first-order equation,

$$-\ln(1-\alpha)=kt,$$

where α is the fraction of the O_2 complex reacted, k the rate constant, and t the time. The temperature dependence of the rate constants conforms to the Arrhenius rate law; the activation energy (E_a) and pre-exponential factor (A) were calculated by the least square analysis. The rate parameters of **3** were also determined from its DWL curves using the following relation derived by Coats and Redfern:[14]

$$\ln[-\ln(1-\alpha)/T^2]=\ln[(AR/E_a)(1-2RT/E_a)]-E_a/RT,$$

where R is the gas constant and T is the temperature. This method has been reported to suffer little from the particle size distribution in a sample.[15] The rate parameters for Complex **3** obtained from DWL curves agree well with those from IWL measurements (Table 1). The rate parameters of the remaining complexes were determined only from the DWL curves, assuming that the reaction follows the first-order equation. The activation energy and pre-exponential factor are then converted to the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$), respectively, using the following relationships:

$$\Delta H^{\neq}=E_a-RT \text{ and } \Delta S^{\neq}=R[\ln(Ah/\kappa kT)-1],$$

where h is the Planck constant; k the Boltzmann constant; and κ the transmission constant (=1). The kinetic parameters are given in Table 1 together with the rate constants at 335 K (k_{335}) calculated from the rate parameters in order to compare the kinetic stability of cobalt–dioxygen bonding.

From the kinetic study of the solid-state oxygenation of Co(3-X-salen) Barkelew and Calvin[6] have proposed that the reaction proceeds through two steps as

$$\text{Co(3-X-salen)}+O_2 \rightleftarrows \text{Co(3-X-salen)}O_2^* \qquad (5, -5)$$

and

$$\text{Co(3-X-salen)}O_2^*+\text{Co(3-X-salen)} \rightleftarrows [\text{Co(3-X-salen)}]_2O_2 \qquad (6, -6)$$

when the oxygen molecules diffuse freely through the crystal lattice of the Co(3-X-salen) complexes. Assuming that the steady state concentration of Co(3-X-salen)O_2^* and k_5[Co(3-X-salen)]pO_2 is zero in a pure nitrogen atmosphere, the decomposition rate can be written as

$$d[(CoL^4)_2O_2]/dt=-k_{-5}k_{-6}[(CoL^4)_2O_2]/(k_{-5}+k_6[CoL^4]),$$

where Co(3-X-salen) is further abbreviated as CoL^4.

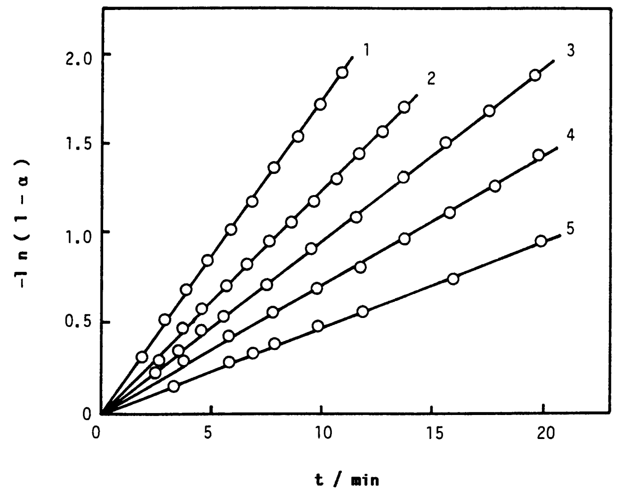

Fig. 2. First-order rate plots for the oxygen dissociation reaction of $[Co(3\text{-}OC_2H_5\text{-salen})]_2O_2$ in a flowing nitrogen atmosphere.
1; 338.6 K, 2; 335.9 K, 3; 334.5 K, 4; 332.5 K, 5; 330.1 K.

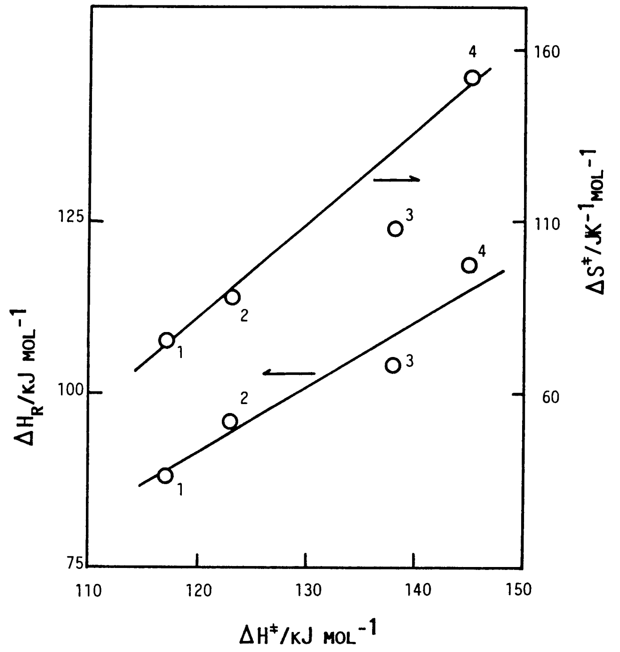

Fig. 3. Plots of the heat of reaction (ΔH_r) and the entropy of activation ($\Delta S^{\neq}_{335}$) against the enthalpy of activation ($\Delta H^{\neq}_{335}$).

When $k_6[\mathrm{CoL}^4] \ll k_{-5}$, the rate becomes first order with respect to $(\mathrm{CoL}^4)_2\mathrm{O}_2$,

$$\mathrm{d}[(\mathrm{CoL}^4)_2\mathrm{O}_2]/\mathrm{d}t = -k_{-6}[(\mathrm{CoL}^4)_2\mathrm{O}_2].$$

Therefore, the rate parameters obtained correspond to Process −6 where a one-electron reduction of the Co(III) ion by the peroxo anion and a cleavage of one cobalt–dioxygen bonding occur. Although Barkelew and Calvin have not mentioned anything concerning the chemical nature of Co(3-X-salen)O_2*, it is speculated that the species is hyperoxocobalt(III) on the basis of solution equilibrium studies of similar systems.[12]

As Table 1 shows, the activation enthalpies decrease in the order of X: $\mathrm{OCH_3} > \mathrm{OC_2H_5} > \mathrm{H} > \mathrm{NO_2}$. In Fig. 3 the heat of reaction and activation entropy are plotted against the activation enthalpy. A linear correlation is observed between the activation enthalpy and the heat of reaction. This seems to be reasonable since the activation energy is associated with the energetic feature of the rapture of cobalt–dioxygen bonding. The kinetic stability, however, does not correlate with the magnitude of the heat of reaction: the calculated k_{355} values decrease in the order of X: $\mathrm{NO_2} > \mathrm{H} > \mathrm{OCH_3} > \mathrm{OC_2H_5}$, and the kinetic stabilities of Complexes **1**, **3**, and **4** are comparable, while that of Complex **3** is exceptionally low. In Complexes **1**, **3**, and **4** the activation entropy increases with increasing activation enthalpy; that is, a kinetic compensation effect is observed. Thus, an increase in the activation enthalpy does not bring about a significant difference in the kinetic bond stability, since it is compensated by an increase in the activation entropy. The $\Delta S^{\neq}$ value for Complex **3** is fairly smaller than that expected from the linear relation, thus accounting for the relatively high kinetic bond stability of **3**. It is not clear what causes such an unexpected stability of this complex; one plausible explanation seems to lie in a crystal-packing effect. The importance of this effect for the solid-state stability of dioxygen complexes was first suggested by Landels and Rodley[16] regarding the isolation of Co(bzacen)(base)O_2 complexes and a disparity between the thermodynamic and kinetic bond stabilities in these complexes has been reported,[17] though a paucity of their crystal structural data made it impossible to assess the crystal-packing effect in these complexes. The crystal-packing effect has been exemplified through the structural analysis of hyperoxocobalt(III) complexes with the ligand of "salen" derivatives, where hydrophobic interactions exist between a coordinated dioxygen ligand and neighboring hydrogen atoms.[18]

Since the intramolecular redox reaction is characteristic for the thermal decomposition of Co(III) complexes, it seems of interest to compare these kinetic features with those of other cobalt(III) complexes. The Co(5-X-salen)NO, X=H, Me, Cl, and $\mathrm{NO_2}$ liberate NO to reproduce the Co(5-X-salen) complexes upon heating. These complexes have the Co(III)–$\mathrm{NO^-}$ bonding unit, and cleavage of the Co–NO bond is accompanied by a one electron redox reaction. The activation enthalpies of the reaction have been reported to be around 120 kJ mol^{-1}, irrespective of the nature of X;[2] they are moderately lower than those of the present deoxygenation reactions. If the activation enthalpy is mainly determined by the reducing power of the reductant, the present results indicate that the reducing power of superoxo group is weaker than that of the $\mathrm{NO^-}$ group and, as expected, the standard electrode potential of the $\mathrm{O_2^-}/\mathrm{O_2^{2-}}$ couple (1.50V) is fairly higher than that of the $\mathrm{NO}/\mathrm{NO^-}$ couple (0.71 V).[19]

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