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THERMAL CHARACTERIZATION OF NITROGEN MONOXIDE DISSOCIATION REACTIONS OF NITROSYL COMPLEXES IN THE SOLID PHASE. MONONITROSYLCOBALT(III) COMPLEXES WITH MIXED LIGAND TETRADENTATE SCHIFF BASES

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ABSTRACT

Thermal NO dissociation reactions in the solid phase of mononitrosylcobalt(III) complexes with the formula, CoL^4NO (L^4 denotes tetradentate ligands such as bzacen, salen and its $5\text{-}NO_2$, 5-Cl, and 5-Me derivatives **) have been investigated by means of TG, DSC, and pyrolysis gas chromatographic analyses. The complexes eliminated one mole of NO per mole in the 160–300°C range and reproduced CoL^4 complexes which possessed X-ray diffraction patterns similar to those of authentic CoL^4 complexes. The kinetic analyses indicated that the NO dissociation process followed a first-order equation; the activation enthalpy values were 120–124 kJ mol^{-1}, being invariable irrespective of the nature of L^4. The values of heat of NO dissociation, determined by the DSC method were in the range 40–50 kJ mol^{-1}. From these thermochemical data and the data of heat of solution of NO, the NO dissociation energies in solution were calculated to be 52–61 kJ mol^{-1}. The thermal data were discussed in terms of the nature of the Co–NO bond.

INTRODUCTION

Many transition metal nitrosyl complexes have so far been synthesized. The potential interest is thought to be in the elucidation of their crystal and molecular structures for interpreting the electronic and steric features of the metal–NO bond [1]. The reactivity of the coordinated NO group has also been subjected to investigations [2]. As for the thermodynamic and/or kinetic characteristics of the reactions forming or cleaving the metal–NO

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** The following abbreviations are used in this paper; bzacen is *N,N′*-ethylenebis(2-benzoyl-1-methylethylideneaminato); salen, *N,N′*-ethylenebis(salicylidenaminato); $5\text{-}NO_2$-, 5-Cl-, and 5-Me-salen are *N,N′*-ethylenebis(5-nitro-, 5-chloro-, and 5-methylsalicylideneaminato), respectively.

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bond, few investigations have been made for solid-state complexes [3] though several have been made for those in solution [4]. In order to understand the nature of the metal–NO bond in more detail, these physicochemical characteristics need to be known.

In the present work, nitrosylcobalt(III) complexes are subjected to thermodynamic and kinetic investigations of the thermal NO dissociation reactions in the solid phase. The dissociation energies of the Co–NO bond of the complexes both in the solid state and in solution are evaluated and discussed in terms of the nature of the Co–NO bond.

EXPERIMENTAL

Materials

The parent complexes Co(bzacen) and Co(5-X-salen) ($X = H$, NO_2, Cl, and Me) were prepared as described in the literature [5,6]. Their nitrosyl complexes were prepared according to the method in the literature [6,7], with the following modifications: a methanol solution (50 cm^3) containing a Schiff base (10 mmol) was deaerated by flushing N_2 gas into the solution and was then saturated with NO at 0°C. A deaerated methanol solution (25 cm^3) of cobalt(II) acetate tetrahydrate (10 mmol) was added. The mixture was kept at 0°C for 2 h under bubbling NO gas. The nitrosyl complexes thus precipitated were collected on a glass filter and then recrystallized from acetone. These complexes were identified on the basis of the results of elemental analysis, IR spectral and magnetic susceptibility measurements (Table 1).

Measurements

Thermal analysis

The TG and DSC curves were recorded as previously reported [8]. The kinetic analysis of the NO dissociation reactions was made on the isothermal weight-loss curves recorded on a Sinku Riko thermal analyzer (model TGD-3000-RH). Pyrolysis gas chromatography (PGC) was carried out as previously reported [9]. The heat of dissociation of NO was determined from the DSC peak area measurements. The instrument was calibrated against the heat of transition (5.4 kJ mol^{-1}) of potassium nitrate [10].

Powder X-ray diffractograms

These were recorded on a Rigaku Denki Geigerflex diffractometer using Co $K\alpha$ radiation and an iron filter.

TABLE 1

Thermal, magnetic, and IR spectral characteristics of the complexes studied (data measured for the sample obtained after pyrolysis of the nitrosyl complexes are given in the parentheses)

Complex	χ_g [a] (10^{-6} cgs)	ν_{NO} [b] (cm^{-1})	Melting point (°C)	Weight loss (%)		NO determination [c] (molar ratio) [d]
				Found	Calcd.	
Co(bzacen)NO	−0.18	1635		6.90	6.89	0.99
	(6.49)		(310)			
Co(bzacen)	6.90		308			
Co(salen)NO	−0.23	1624		8.60	8.46	1.01
	(7.21)		(350)			
Co(salen)	7.18		352			
Co(5-NO_2-salen)NO	−0.15	1696		6.66	6.72	0.95
	(5.58)					
Co(5-NO_2-salen)	5.36					
Co(5-Cl-salen)NO	−0.08	1638		7.13	7.08	0.95
	(7.23)		(364)			
Co(5-Cl-salen)	6.96		364			
Co(5-Me-salen)NO	−0.15	1614		7.52	7.83	0.98
	(7.03)		(314)			
Co(5-Me-salen)	7.16		314			

[a] Determined at a room temperature, 25°C.

[b] Measure in KBr disk.

[c] Determined by pyrolysis gas chromatography. Conditions: column packing, molecular sieves 5A; column temperature, 50°C; TCD temperature, 70°C; pyrolysis temperature, 250°C; see ref. 9.

[d] NO complex.

Solubility and heat of solution

A sample complex was saturated into benzene or ethanol in an Erlenmeyer flask equipped with a tapered stopper. Nitrogen gas was flushed through the mixture for 0.5 h. Then the mixture was kept at a constant temperature in a thermostatted incubator (±0.05°C). A 5-cm^3 aliquot of the supernatant fraction was pipetted off and was diluted to an appropriate, constant volume with DMF. The concentration of the diluted solution was determined by the measurement of its optical absorbancy and by the calibration curve drawn with solutions dissolving a known amount of the complex in the same solvent as the above diluted solution. The sampling of the fraction was carried out every ca. 24 h until a constant solubility was obtained within the experimental error. Similar measurements were made at several temperatures elevated stepwise.

The heat of solution was calculated by using the following equation

$$\frac{\Delta H_{sol}}{T} = R\left(\frac{\partial \ln X}{\partial \ln T}\right)$$

where ΔH_{sol} is the heat of solution; X, the solubility; R, the gas constant; and T, the temperature [11].

RESULTS

TG, DSC and X-ray diffraction analyses

The thermoanalytical data are summarized in Table 1 along with the magnetic and IR spectral data. The TG and DSC curves are given in Fig. 1. Figure 1a shows that Co(bzacen)NO undergoes three endothermic changes. The change corresponding to the first DSC peak with a maximum at 250°C is accompanied by a weight loss of 6.9% over the 165–280°C range; this weight loss agrees with the calculated value of 6.89%, assuming that one

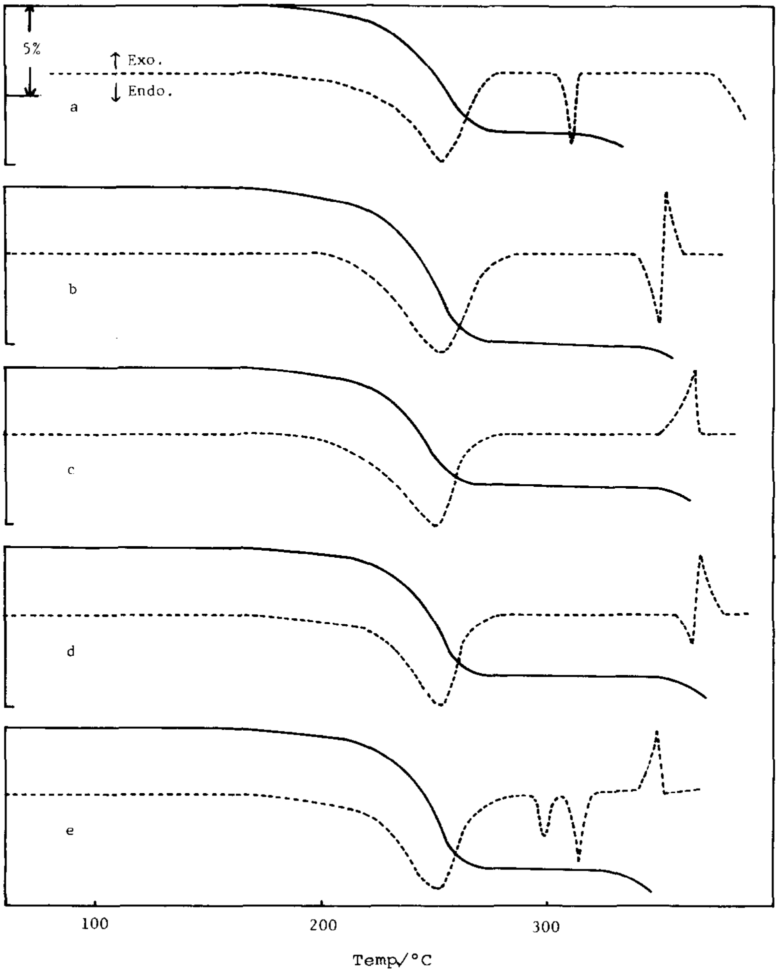

Fig. 1. TG (———) and DSC (- - - - -) curves recorded in a flowing nitrogen atmosphere at a heating rate of 10°C min^{-1}. (a) Co(bzacen)NO; (b) Co(salen)NO; (c) Co(5-NO_2-salen)NO; (d) Co(5-Cl-salen)NO; (e) Co(5-Me-salen)NO. Except for the peaks around 250°C, the DSC curves of the nitrosyl complexes were the same as those of the corresponding authentic parent complexes, which were not reproduced here.

mole of NO is eliminated from one mole of Co(bzacen)NO. The second peak at 310°C, not accompanied by a weight loss, is due to the melting of the resultant Co(bzacen) complex. This temperature agrees with the melting temperature of the authentic Co(bzacen). The decomposition of the resultant complex is initiated at 380°C. For Co(salen)NO and its 5-nitro and 5-chloro derivatives, the thermal behavior is similar to that of Co(bzacen)NO. The Co(5-Me-salen)NO complex behaves somewhat differently from the above nitrosyl complexes; its NO elimination leaves behind a complex which shows two endothermic DSC peaks with maxima at 298 and 314°C; neither peaks are accompanied by a weight loss. The peak at 298°C could be ascribed to a transformation in the crystal structure and the peak at 314°C due to the melting. The authentic Co(5-Me-salen) complex also underwent two endothermic changes showing the DSC peak at 298°C corresponding to the above transformation and at 314°C due to the melting; both changes caused no weight loss.

Since the NO group in several nitrosyl compounds has been reported to be converted, on pyrolysis, into N_2 and/or N_2O [12], it is desirable to analyze the gaseous product yielded from the nitrosyl complexes. Therefore, the PGC analysis was carried out under the conditions cited in the footnote of Table 1 to determine N_2, N_2O and NO gases. The results indicate the stoichiometric reproduction of NO as seen in Table 1. Thus, the thermal

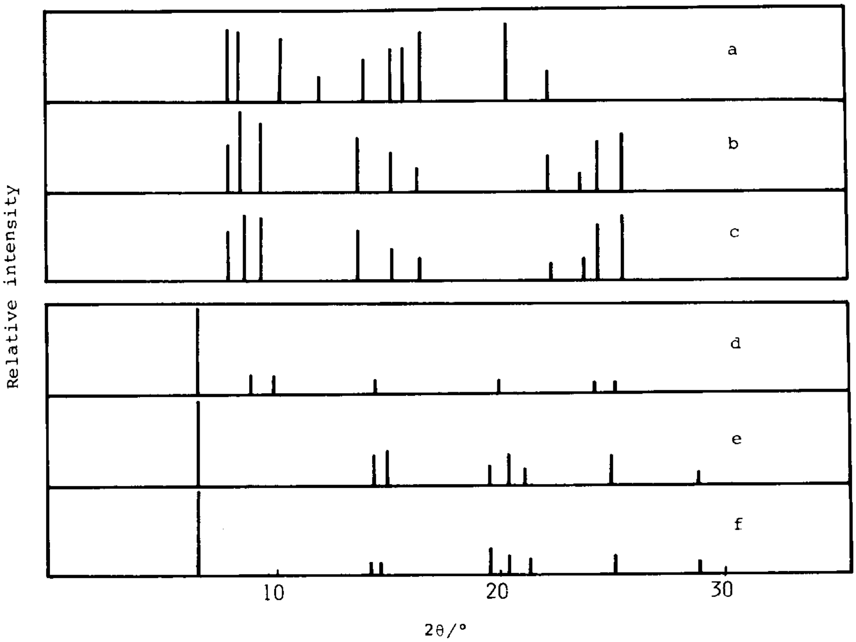

Fig. 2. Comparison of powder X-ray diffractograms for the nitrosyl and corresponding parent complexes. (a) Co(bzacen)NO; (b) Co(bzacen) obtained by pyrolysis; (c) authentic Co(bzacen); (d) Co(salen)NO; (e) Co(salen) obtained by pyrolysis; (f) authentic Co(salen).

reaction of the present complexes can be described as follows

$$CoL^4NO(crystal) \rightarrow CoL^4(crystal) + NO(gas)\uparrow \quad (1)$$

As described above, the melting temperatures of the complexes obtained by the dissociation of NO from the nitrosyl complexes coincided with those of the corresponding, authentic parent complexes (Table 1). This indicates that the NO dissociation of the CoL^4 crystals is accompanied by the reproduction of CoL^4 with a crystalline state similar to those of authentic CoL^4. This was also confirmed by the fact that the X-ray diffractograms of the crystals obtained by the NO dissociation of the nitrosyl complexes corresponded to those of the authentic parent complexes. An example is shown in Fig. 2.

Kinetic analysis

The kinetics of the NO dissociation were analyzed on the basis of the isothermal weight-loss curves. For all the complexes, the dissociation process was found to fit the first-order equation well: $-\ln(1-\alpha) = kt$ (α is the conversion; k, the rate constant; and t, the time). The results of the rate plots are shown in Fig. 3 for the case with Co(bzacen)NO. The kinetic data are tabulated in Table 2.

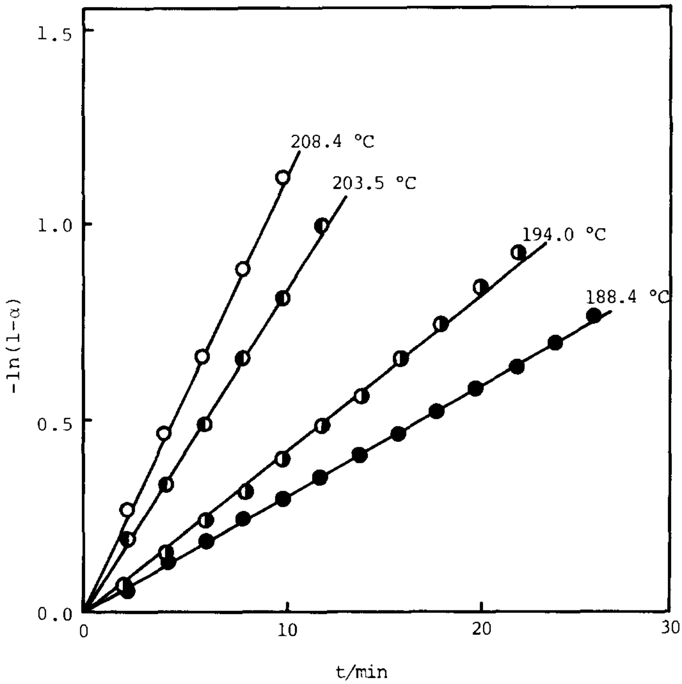

Fig. 3. First-order rate plots for the NO dissociation of Co(bzacen)NO.

TABLE 2

Kinetic parameters for thermal NO dissociation

Complex	k (10^{-4} s^{-1})	Temp. (°C)	$\Delta H^{\neq}$ [a] (kJ mol^{-1})	$\Delta S^{\neq}$ [b] (J mol^{-1} K^{-1})
Co(bzacen)NO	17.8	208.4	124 ± 1	−52 ± 2
	13.2	203.5		
	6.93	194.0		
	3.62	188.4		
Co(salen)NO	1.57	177.8	124 ± 10	−56 ± 25
	0.933	172.8		
	0.700	167.7		
	0.467	162.3		
Co(5-NO_2-salen)NO	1.85	188.0	120 ± 7	−67 ± 16
	1.68	185.1		
	0.917	177.9		
	0.600	170.3		
	0.433	167.8		
Co(5-Cl-salen)NO	1.72	178.3	121 ± 7	−60 ± 8
	1.11	173.3		
	0.733	167.7		
	0.533	162.6		
Co(5-Me-salen)NO	8.17	208.8	121 ± 7	−64 ± 8
	3.10	193.2		
	2.35	188.1		
	1.73	183.9		

[a] Determined from a least-squares analysis of Arrhenius plots.

[b] Obtained from the equation: $\Delta S^{\neq} = R(\ln A - \ln kT/h - 1)$, where R is the gas constant; A, the Arrhenius factor; k, the Boltzman constant; T, the temperature; and h, the Planck constant.

DISCUSSION

The nitrosyl complexes examined here thermally dissociate NO quantitatively and the reaction is accompanied by a change in the crystalline state for a pair of the nitrosyl and one of its parent complexes. These facts allow the thermodynamic character regarding the Co–NO bond to be estimated. The enthalpy change of reaction (1), denoted here as ΔH^{cry}, is in the range 40–54 kJ mol^{-1}. These ΔH^{cry} values are composed of the values due to two energy terms, i.e., the Co–NO bond energy and the difference in the lattice energy between a given pair of the nitrosyl and one of its parent complex crystals. Most of the thermodynamic investigations have been carried out by determining the formation or dissociation constants in solution. Therefore, we attempt to reduce the ΔH^{cry} values to solution data as above. The ΔH_{diss} value, the assumptive enthalpy change of the NO-dissociation reaction in solution (eqn. 2), can be evaluated by using the following equations

$$CoL^4NO(crystal) = CoL^4(crystal) + NO(gas)\uparrow + \Delta H^{cry}$$

$$\mathrm{CoL^4NO(crystal)} = \mathrm{CoL^4NO(solution)} + \Delta H_{\mathrm{sol}}(\mathrm{CoL^4NO})$$

$$\mathrm{CoL^4(crystal)} = \mathrm{CoL^4(solution)} + \Delta H_{\mathrm{sol}}(\mathrm{CoL^4})$$

$$\mathrm{NO(gas)} = \mathrm{NO(solution)} + \Delta H_{\mathrm{sol}}(\mathrm{NO})$$

$$\mathrm{CoL^4NO(solution)} = \mathrm{CoL^4(solution)} + \mathrm{NO(solution)} + \Delta H_{\mathrm{diss}} \qquad (2)$$

In these equations, ΔH_{sol} represents the heat of solution of the compound given in the parentheses. From these relations, ΔH_{diss} is represented as

TABLE 3

Thermochemical characteristics

Complex	ΔH^{cry} [a] (kJ mol^{-1})	Solubility [b] (10^{-1} mol l^{-1})	Solvent	Wave-length (nm)	$\Delta H_{\mathrm{sol}}^{\mathrm{cry}}$ [c] at 298 K (kJ mol^{-1})	ΔH_{diss} [d] (kJ mol^{-1})
Co(bzacen)		1.55 (30.00)	Benzene	386	30.3	
		1.85 (35.18)				
		2.34 (40.43)				
		3.05 (44.82)				
Co(bzacen)NO	50	1.22 (30.00)	Benzene	386	24.1	52
		1.45 (35.18)				
		1.71 (40.73)				
		1.97 (44.82)				
Co(salen)		1.11 (26.50)	Ethanol	387	18.7	
		1.18 (30.48)				
		1.42 (36.02)				
Co(salen)NO	54	15.6 (30.42)	Ethanol	387	11.0	59
		17.7 (35.22)				
		18.7 (40.40)				
Co(5-Cl-salen)		0.140 (30.19)	Benzene	395	27.1	
		0.157 (35.48)				
		0.193 (39.07)				
		0.213 (42.10)				
Co(5-Cl-salen)NO	53	5.65 (28.15)	Benzene	395	18.2	58
		7.20 (35.48)				
		7.39 (39.07)				
		7.91 (42.10)				
Co(5-Me-salen)		0.481 (30.48)	Ethanol	385	44.2	
		0.669 (35.16)				
		0.724 (36.02)				
Co(5-Me-salen)NO	51	8.41 (30.11)	Ethanol	385	31.9	61
		11.1 (35.22)				
		11.4 (36.02)				
Co(5-NO_2-salen)NO	40					

[a] Determined from the DSC peak area measurements.

[b] Temperature (°C) given in parentheses.

[c] Heat of solution at 298 K.

[d] Calculated from eqn. (3).

follows

$$\Delta H_{\text{diss}} = \Delta H^{\text{cry}} - \Delta H_{\text{sol}}(\text{CoL}^4\text{NO}) + \Delta H_{\text{sol}}(\text{CoL}^4) + \Delta H_{\text{sol}}(\text{NO}) \qquad (3)$$

The observed ΔH_{sol} values for the complex crystals in benzene or ethanol are given in Table 3. The ΔH_{sol}(NO) values in benzene or ethanol at 298 K have been reported to be -3.9 and -2.5 kJ mol^{-1}, respectively [13]. Thus, ΔH_{diss} values for the present nitrosyl complexes are calculated to be 52–61 kJ mol^{-1} (Table 3). The fact that the ΔH_{diss} values have fallen in the above narrow range is thought to reflect on the Co–NO bond character.

As for Co(bzacen)NO and Co(salen)NO it has been established by X-ray crystal structure analysis that the NO group is bound to the Co atom in such a manner that it possesses a bent Co–N–O linkage; the Co–N–O angle is 122.9° for the former [14] and 127° for the latter [15]. With respect to the other nitrosyl complexes examined here, these are thought to include the NO group in the same manner, since their thermal NO dissociation reactions occurred analogously to those above. The bonding of NO to Co in a bent manner is generally understood as follows [16]: one electron transferring from the low-spin Co(II) atom to NO results in the formation of Co(III) and an NO$^-$ group; the resulting NO$^-$ group datively binds Co(III) utilizing one of the lone pairs of the sp^2 hybrid orbitals of the N atom. Thus, the bonding may actually be understood by delineating as Co(III)–NO$^-$. Moreover, the Co(III)–NO$^-$ bonding is considered to call for the participation of the $d\pi$–$p\pi$(NO$^-$) back bonding, since the Co–(N) bond distance 1.81–1.87 Å is shorter than the single Co–N bond distance 1.95–1.96 Å known for dative Co(III)–N bonds [17]. As for Co(bzacen)NO, investigations by X-ray photoelectron spectroscopy supported the presence of Co(III)–NO$^-$ bonding in the complex [18]. The IR stretching frequency ν_{NO} has often been taken as a qualitative indication of the extent of the $d\pi$–$p\pi$ interaction [19]. Table 1 shows that the substitution of the electron donating groups on the aryl rings shifts ν_{NO} towards a lower energy. This indicates that these substituents tend to increase the extent of the $d\pi$–$p\pi$(NO$^-$) interaction. On the other hand, it is not unreasonable to expect that the above substituents weaken the Lewis acidity of the Co(III) atom and hence weaken the dative bonding from the NO$^-$ group to the Co(III) atom [20]. With respect to the ΔH_{diss} values that fall in the narrow range, irrespective of the nature of the L^4 ligands, this can be explained since in the Co(III)–NO$^-$ bonding the increase in the $d\pi$–$p\pi$ bond character is compensated by a decrease in the dative σ-bond character. It should be pointed out that ΔH_{diss} values (52–61 kJ mol^{-1}) for the present nitrosyl complexes are found to be larger than the enthalpy change (33 kJ mol^{-1}) of the dissociation reaction of Co$^{\text{II}}$(salen)py into Co$^{\text{II}}$(salen), and py in chloroform [21]. This fact appears to be in line with the consideration that the present nitrosyl complexes include the Co(III)–NO$^-$ bonding.

The mode of the Co(III)–NO$^-$ bonding resembles that of the Co(III)–O$_2^-$ bonding produced by the reaction of the low-spin, square-planar Co(II) complexes with molecular oxygen [22]. Therefore, it is thought to be quotable for comparison that the enthalpy changes of the O_2 dissociation reactions of CoL^4BO_2 type complexes in toluene (L^4 is bzacen and B is an organic base) are 55–76 kJ mol^{-1} [23]. These are in a similar range to those of the ΔH_{diss} values (55–61 kJ mol^{-1}) of the nitrosyl complexes.

Since the NO dissociation reactions of the complexes in the solid phase fit the first-order equation, the kinetic data of these reactions may be compared with each other. As has been discussed, the complexes are considered to include the Co(III)–NO^- bond, hence NO dissociation reactions are accompanied by a concomitant electron transfer. A probable scheme is described as follows

$$\text{Co(III)–NO}^- \rightarrow \text{Co(II)–NO} \rightarrow \text{Co(II)} + \text{NO}$$

Quantitative NO recovery is not possible if the Co(III)–NO^- bond cleavage precedes the electron transfer. We suppose that the Co(II)–NO bond cleavage process is faster than the electron transfer process since the Co(II)–N dative bonding seems to be thermally unstable [24]. Thus it is thought that the NO dissociation rate is determined by the electron transfer process and the observed $\Delta H^{\neq}$ values in Table 3 are dominated by the energy for the electron transfer. As for some intramolecular electron transfer reactions in Co(III) complexes, the activation enthalpy values are reported to be negative [25]. It does not seem to be contrary to the present results that negative $\Delta S^{\neq}$ values were observed for the NO dissociation reactions.

REFERENCES

1 J.H. Enermark and R.D. Feltman, Coord. Chem. Rev., 13 (1974) 339.
2 J.A. Macleverty, Chem. Rev., 79 (1979) 53.
3 F. Rallo and P. Silverstroni, Ric. Sci., 3 (1963) 1001; Chem Abstr., 60 (1964) 7668h.
4 R.T.M. Fraser, J. Inorg. Nucl. Chem., 17 (1961) 265.
5 P.J. MaCarty, R.J. Hovey, K. Ueno and A.E. Martell, J. Am. Chem. Soc., 77 (1955) 5820.
6 A. Earnshow, P.C. Hewlett and L.F. Larkworthy, J. Chem. Soc., (1965) 4718.
7 M. Tamaki, I. Masuda and K. Shinra, Bull. Chem. Soc. Jpn., 42 (1969) 2858.
8 K. Miyokawa, H. Hirashima and I. Masuda, Bull. Chem. Soc. Jpn., 54 (1981) 3361.
9 (a) K. Miyokawa, H. Masuda and I. Masuda, Bull. Chem. Soc. Jpn., 53 (1980) 3573; (b) K. Miyokawa, N. Abe and I. Masuda, J. Inorg. Nucl. Chem., 43 (1981) 2791; (c) Bull. Chem. Soc. Jpn., 55 (1982) 3647.
10 Kagaku Binran Kisohen, the Chemical Society of Japan, Maruzen, Tokyo, 1975, p. 412.
11 J.H. Hildebrand, J. Chem. Phys., 20 (1952) 190.
12 W.R. Moser, The Catalytic Chemistry of Nitrogen Oxide, Plenum, New York, 1975, p. 33; ref. 9a and b.
13 Gmeline Handbuch der Anorganishen Chemie, 8 Auflage, Verlag Chemie, GmbH, Weiheim/Bergstrasse, 1968, p. 706.
14 R. Wiest and R. Weiss, J. Organomet. Chem., 30 (1971) C33.
15 K.J. Haller and J.H. Enemark, Acta Crystallogr., Sect B, 34 (1978) 102.
16 D.A. Snyder and D.L. Weaver, Inorg. Chem., 9 (1970) 2760; C.S. Pratt, B.A. Coyle and J.A. Ibers, J. Chem. Soc. A, (1971) 2146.

17 W.R. Scheidt and J.L. Horard, J. Am. Chem. Soc., 95 (1973) 8281.
18 J.W. Lauher and J.E. Lester, Inorg. Chem., 12 (1973) 244.
19 R.F. Fenks and R.L. Dekok, Inorg. Chem., 11 (1972) 437.
20 H. Masuda, T. Kawarada, K. Miyokawa and I. Masuda, Thermochim. Acta, 63 (1983) 307.
21 E. Cesarotti, M. Gullotti, A. Pasini and R. Ugo, J. Chem. Soc., Dalton Trans., (1977) 757.
22 S. Koda, A. Misono and Y. Uchida, Bull. Chem. Soc. Jpn., 43 (1970) 3143.
23 M.J. Carter, D.P. Rillema and F. Basolo, J. Am. Chem. Soc., 96 (1974) 392.
24 W.W. Wendlandt and J.P. Smith, J. Inorg. Nucl. Chem., 25 (1963) 1267; W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 545.
25 H. Taube, Tunneling in Biological Systems, Academic Press, New York, 1979, p. 173.