

Thermolysis of Alkyl(aquo)- and Alkyl(pyridine)cobaloximes in the Solid State. Influence of the Alkyl Group on Axial Cobalt–Ligand Bond Stability and Correlation with Solution Properties

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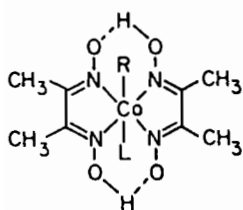
(Received September 12, 1986)

Abstract

The solid state thermolysis of a series of 24 organo(aquo)cobaloximes and 19 organo(pyridine)cobaloximes has been investigated by differential scanning calorimetry and thermogravimetric analysis. In the most favorable cases three distinct transitions are observed by both techniques which may be assigned to loss of the axial (aquo or pyridine) ligand, loss of the organic ligand, and decomposition of the 'core' bis(dimethylglyoximate)cobalt complex. The temperatures for the first transition for the aquo complexes correlate reasonably well with the Taft polar substituent constant, σ^* . In addition, a number of highly significant correlations were found between the temperature of the first transition and rate constants for ligand exchange processes in solution.

Introduction

The carbon–cobalt bond in organocobalt complexes is now known to be stabilized by a wide variety of equatorial ligand systems [1]. Thermolytic aspects involving the axial ligands are less well understood, particularly from a solid-state chemistry perspective. In this paper, we describe thermal studies by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of two extensive series of $\text{RCo}(\text{D}_2\text{H}_2)\text{L}[\text{D}_2\text{H}_2 = \text{bis}(\text{dimethylglyoximate})]$ equatorial ligand, $\text{L} = \text{H}_2\text{O}$, **1**, or pyridine,



- 1** $\text{L} = \text{H}_2\text{O}$
2 $\text{L} = \text{pyridine}$

2] compounds. In particular, we focus on the *trans* effect (*cf.* ref. 2) of the R group on the solid-state thermal deaquation and depyridination of **1** and **2** respectively, and on the correlation of the characteristic temperatures associated with these reactions with pertinent solution properties. Few reports exist on these aspects, and the information that currently exists is restricted to a very limited compound series containing almost exclusively pyridine as the axial ligand and *N,N'*-ethylenebis(salicylideneamine) as the equatorial ligand system [3–7]. Sulfite-complexes of Co containing D_2H_2 , however, have been recently studied [8]. A brief examination of the thermal behavior of organocobalt complexes containing a variety of chelating equatorial ligands has also recently appeared [9].

The electronic influence of the R group has been quantified in these previous studies, in terms of correlations of the Taft polar substituent constant, σ^* [10–12], with the activation energy [3], enthalpy [4], or rate constant [4, 6] corresponding to the thermal dissociation of the Co–L bond. However, extraction of these latter thermodynamic and kinetics parameters from DSC and TGA experiments is handicapped by the need for rather extensive data manipulation and questionable assumptions as to the validity of a particular kinetics model. The latter difficulty is known to be particularly severe with solid-state thermal processes [13]. For these reasons, we have opted to utilize herein, characterize DSC and TGA temperatures corresponding to the deaquation or depyridination reactions, for correlation with σ^* . This sort of correlation has an interesting parallel with the Zuman plotting protocol (*i.e.*, plot of the electrochemical oxidation or reduction potential *versus* σ^*) which is employed in electrochemical methodology [14].

We also attempt to illustrate below how shifts in the characteristic deaquation and depyridination temperatures with the nature of the R group, cannot be solely ascribed to the electronic influence exerted by the latter. Steric (and possibly other unknown) factors play a complicating role and, unlike in

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previous studies on a limited series of compounds [3–7], these complications are particularly evident in the cases examined herein.

Experimental

DSC and TGA experiments were performed on a DuPont Model 1090 Thermal Analysis System fitted with the Models 910 and 953 accessory modules respectively. The software supplied by the manufacturer was used for the most part for data analyses. All measurements were performed in the dark (to preclude photolysis of the compounds) and in a dynamic (*ca.* 80 ml/min) inert gas atmosphere (usually Ar). A nominal heating rate of 10 °C/min was employed for the nonisothermal measurements. Sealed Al pans were used for DSC; the samples were held in an open Pt boat for TGA. In the correlations of DSC and TGA characteristic temperatures presented below, this difference in sample containment geometry and sensor location will have to be borne in mind. The sample mass was in the 1–5 mg range in both cases. Indium was used as the calibration standard for temperature and enthalpy measurements in DSC. Calcium oxalate monohydrate was used for calibrating the TGA system.

The majority of the thermal data (*i.e.*, enthalpies and characteristic temperatures) presented below are those averaged from replicate (at least three) runs. The enthalpies have a relative uncertainty of $\pm 3\%$ and temperatures are accurate to within ± 2 °C in DSC and ± 4 °C in TGA based on calibration data. The precision in individual cases, however, does depend on other factors (*e.g.*, compound volatility) (*vide infra*).

Organo(aquo)cobaloximes were synthesized by standard reductive alkylation methods [15] and characterized by ^1H NMR, thin-layer chromatography, and elemental analyses. Organo(pyridine)cobaloximes were obtained from the aquo complexes by addition of excess pyridine to methanolic solutions followed by addition of water and concentration. The yellow precipitates were filtered, dried in vacuum over P_2O_5 , and characterized as above.

Results and Discussion

Figures 1–3 illustrate representative DSC and TGA scans for alkyl(aquo)cobaloximes, $\text{RCo}(\text{D}_2\text{H}_2)\text{-OH}_2$. Thermal data for 24 compounds are summarized in Tables I (DSC) and II (TGA). About half of the compounds studied showed three clearly separated transitions by both techniques, as exemplified by the DSC and TGA traces in Figs. 1a and 1b respectively for $\text{R} = \text{CH}_3\text{CH}_2$. Within the constraints outlined in 'Experimental', values of the characteris-

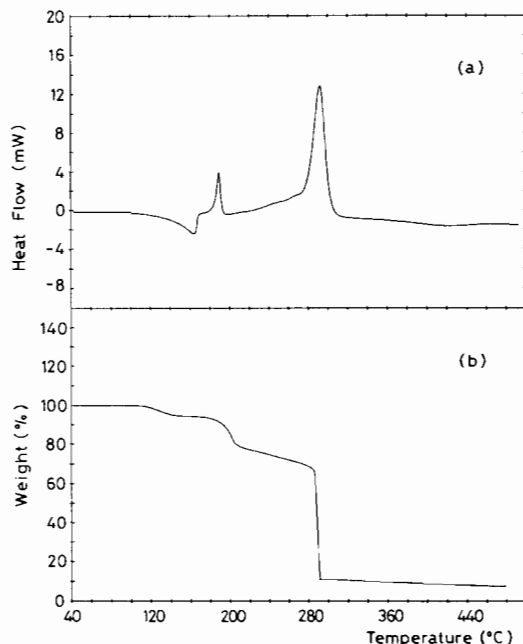


Fig. 1. Differential scanning calorimetry (DSC) (a) and thermogravimetric analysis (TGA) (b) scans for an alkyl(aquo)cobaloxime [$\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$] sample ($\text{R} = \text{CH}_3\text{CH}_2$) illustrating three clearly resolved T_1 , T_2 and T_3 transitions.

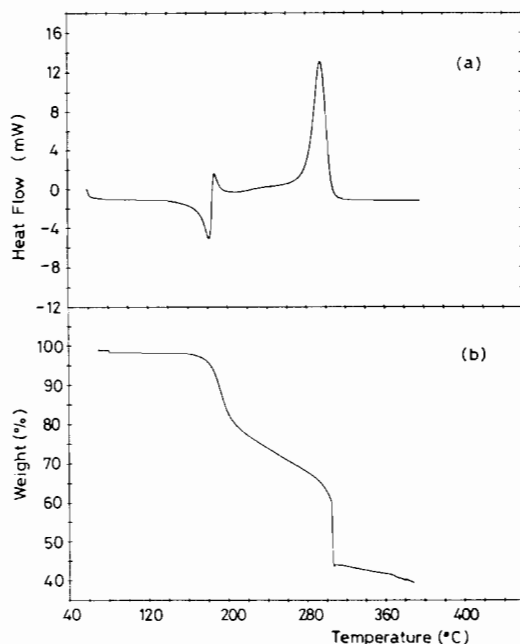


Fig. 2. DSC (a) and TGA (b) traces for $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ ($\text{R} = \text{CH}_3\text{OOCCH}_2$) exemplifying overlapped T_1 and T_2 transition regimes.

tic temperatures for the various transitions agreed well between the two techniques. These characteristic temperatures are taken as the peak temperature of the endotherm (or exotherm) in the DSC scan and

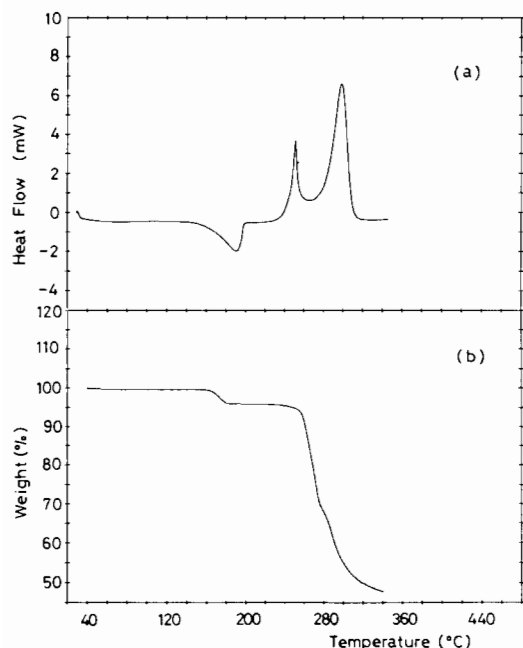


Fig. 3. DSC (a) and TGA (b) traces for $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ ($\text{R} = m\text{-CH}_3\text{OCC}_6\text{H}_4$) illustrating overlapped T_2 and T_3 transition regimes.

the inflexion point of the weight-loss curve in the TGA trace. The three transitions are interpreted as being due to loss of the axial water ligand (T_1), loss of the axial organic ligand (T_2 , probably as RH), and finally decomposition of the 'core' complex (*i.e.*, bis(dimethylglyoximato)cobalt, T_3). These assignments are supported by several observations. First, if the data for $\text{R} = (\text{CH}_3\text{CH}_2)_2\text{CH}$, which showed a gradual weight loss across the T_1 – T_2 region with no clear T_2 transition, are omitted, the average weight loss accompanying the T_1 transition ($N = 12$) was $102 \pm 9\%$ of that calculated for loss of axial water. Second, although the weight loss data for the T_2 transition has an average value ($N = 9$) of 125% of that calculated for loss of the axial organic ligand (as RH), there is a clear, if somewhat variable, trend for this value to increase with increasing T_2 throughout the series. This suggests a significant, but variable, volatility of the $\text{RCo}(\text{D}_2\text{H}_2)$ fragment giving rise to the high T_2 weight loss values. Third, the T_3 transition, which should be the same for all compounds as it involves only the common 'core' complex, occurs at virtually the same temperature for each complex ($T_3 = 292 \pm 5$ °C, $N = 23$, by DSC, $T_3 = 285 \pm 10$ °C, $N = 14$, by TGA). Finally, the enthalpy associated with the thermal breakdown of the 'core' complex

TABLE I. Differential Scanning Calorimetry (DSC) Data for Alkyl(aquo)cobaloximes, $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$

Compound	R	T_1 (°C)	ΔH_1^a (kJ/mol)	T_{overlap} (°C)	T_2 (°C)	ΔH_2^a (kJ/mol)	T_3 (°C)	ΔH_3^a (kJ/mol)
1a	$(\text{CH}_3)_3\text{SiCH}_2$	138	59		201	–83	290	
1b	$\text{CH}_3(\text{CH}_2)_5$	136	38		150		293	
1c	$(\text{CH}_3\text{CH}_2)_2\text{CH}$	139	60		– ^b		286	
1d	$(\text{CH}_3)_2\text{CH}$			141			292	–338
1e	CH_3CH_2	164	51		190	–27	292	–395
1f	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	142	10		159	30	295	–361
1g	$\text{CH}_3\text{CH}(\text{OCH}_3)\text{CH}_2$			136			284	
1h	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$			144			283	–352
1i	HOCH_2CH_2			182			289	
1j	$\text{NC}(\text{CH}_2)_3$	128	24		228		294	
1k	$\text{CH}_3\text{OCH}_2\text{CH}_2$			155			282	
1l	$\text{CH}_3\text{CH}=\text{CH}$	172	36		194		290	–308
1m	$\text{CH}_3\text{OOCCH}_2\text{CH}_2$	141	32		152		293	
1n	$\text{HOOCCH}_2\text{CH}_2$			164			292	–307
1o	ICH_2			168			294	
1p	$m\text{-CH}_3\text{OCC}_6\text{H}_4$	190	61		252		298	
1q	$p\text{-CH}_3\text{OCC}_6\text{H}_4$	188	57		252		296	
1r	CH_3CH_2			186			296	–339
1s	$p\text{-CH}_3\text{COC}_6\text{H}_4$	180	64		– ^c		294	–383
1t	$p\text{-CF}_3\text{C}_6\text{H}_4$	164	19		181		296	–343
1u	ClCH_2	176	52		207		292	
1v	$\text{CH}_3\text{OOCCH}_2$			182			295	–326
1w	$\text{CH}_3\text{CH}_2\text{OOCCH}_2$			176			293	–296
1x	CH_3	150	54		248		289	

^aEnthalpies are reported only in those cases where the transitions are clearly resolved. Exothermic cases are denoted by a negative sign. ^bNo sharp transition was observed. ^cThe T_2 transition was poorly developed.

TABLE II. Thermogravimetric Analysis (TGA) Data for Alkyl(aquo)cobaloximes, RCo(D₂H₂)OH₂

Compound	R	T_1 (°C)	Weight loss ^a	T_2 (°C)	Weight loss ^b	T_{overlap} (°C)	Weight loss ^c	T_3^d (°C)
1a	(CH ₃) ₃ SiCH ₂	126	102	209	131			284
1b	CH ₃ (CH ₂) ₅	113	115	289	124			289
1c	(CH ₃ CH ₂) ₂ CH	120	207 ^e	— ^e	— ^e			265
1d	(CH ₃) ₂ CH					129	96	— ^f
1e	CH ₃ CH ₂	141	104	191	190			267
1f	C ₆ H ₅ CH ₂ CH ₂					148	100	288
1g	CH ₃ CH(OCH ₃)CH ₂					137	81	281
1h	CH ₃ CH ₂ OCH ₂ CH ₂					148	99	294
1i	HOCH ₂ CH ₂					185	96	277
1j	NC(CH ₂) ₃	132	109	230	144			285
1k	CH ₃ OCH ₂ CH ₂					154	106	281
1l	CH ₃ CH=CH	156	98	213	173			289
1m	CH ₃ OOCCH ₂ CH ₂	123	120	152	111			288
1n	HOOCCH ₂ CH ₂					173	111	292
1o	ICH ₂					175	154	— ^f
1p	<i>m</i> -CH ₃ OOC ₆ H ₄	173	88	273	88			272
1q	<i>p</i> -CH ₃ OOC ₆ H ₄	168	95	267	58			287
1r	CF ₃ CH ₂					193	102	284
1s	<i>p</i> -CH ₃ COC ₆ H ₄	186	99	— ^g	— ^g			294
1t	<i>p</i> -CF ₃ C ₆ H ₄	145	101	— ^h	— ^h			288
1u	ClCH ₂	167	102	214	102			— ^f
1v	CH ₃ OOCCH ₂					188	81	304
1w	CH ₃ CH ₂ OOCCH ₂					186	121	— ^f
1x	CH ₃	149	97	248	— ^f			— ^f

^aWeight loss expressed as percent of value calculated for loss of axial H₂O. ^bWeight loss expressed as percent of value calculated for loss of axial R as RH. ^cWeight loss expressed as percent of value calculated for loss of both axial H₂O and axial RH. ^dNo weight loss reported because of uncertainty induced by excessive compound volatility at this temperature. ^eShowed gradual weight loss without a well defined T_2 transition. ^fNo clear T_3 transition was observed, apparently due to excessive weight loss at T_2 . ^gNo T_2 transition was observed. ^h T_2 transition was poorly developed.

is fairly constant across both the aquo and the pyridine series (see below) at -345 ± 50 kJ/mol ($N = 17$). The rather large magnitude of uncertainty associated with the determination of this enthalpy value can be traced to the volatility problem referred to previously.

For those compounds for which only two transitions were observed (as typified in Fig. 2), it is quite clear that the lower transition represents the overlap of the T_1 and T_2 processes while the upper process represents the decomposition of the 'core' complex (T_3). This is evident from the fact that the average observed weight loss as a percentage of the value calculated assuming the loss of both the axial water and organic ligands was 104% ($N = 11$). In addition, the average values of the upper temperature transition for these compounds (290 ± 5 °C, $N = 9$, by DSC, 288 ± 10 °C, $N = 6$, by TGA) agree well with the average value of T_3 for those compounds showing three clean transitions (294 ± 4 °C, $N = 12$, by DSC, and 283 ± 11 °C, $N = 8$, by TGA).

Figure 2 contains examples of DSC and TGA scans which show overlap of the deaquation and dealkylation transition regimes. Cases wherein the latter

process overlaps with the T_3 transition are exemplified by the traces shown in Fig. 3. The overall pattern of the thermolysis of these compounds, *i.e.* deaquation < dealkylation < 'core' complex breakdown, is similar to the observations of previous authors [3–9] on other organocobalt complexes. The RCo(salen)L system, however, appears to reveal a significantly better degree of resolution between the three transition regimes *vis-a-vis* the compounds studied here (*cf.* refs. 3–7).

For cases such as those illustrated in Figs. 2 and 3, attempts were made to enhance resolution, either by lowering the heating rate or by the use of a high thermal conductivity purge gas such as He. In selected instances, either of these strategies afforded satisfactory results [16]. However, the characteristic temperatures shift appreciably as a result of varying the purge gas or the heating rate. This difficulty, coupled with the less than complete degree of success for all the cases tested, hampered our efforts to use such data for the correlations described below.

Numerous attempts were made to correlate the thermal data in Tables I and II with other properties of the alkyl(aquo)cobaloximes. For instance, many

solution properties of these compounds involving axial ligand substitution, have been shown [17, 18] to correlate well with σ^* . If we assume that for those compounds showing only two transitions (e.g., Fig. 2) the overlap temperature accurately reflects the value of T_1 and uses the average of the T_1 values from DSC and TGA as the best estimates, the T_1 values of 20 of the 24 compounds (omitting R = HOCH₂CH₂, NC(CH₂)₃, CH₃OOCCH₂CH₂, and *p*-CF₃C₆H₄) correlate well with σ^* for the organic ligand (Fig. 4, $r^2 = 0.91$). The trend in this correlation is in the anticipated direction, *i.e.* increasing electron withdrawal by the organic ligand increases the strength of interaction of the axial water ligand with the metal center, increasing T_1 . Although there is considerable scatter in this correlation, it is actually surprisingly good considering the wide range of steric bulk of the organic ligands in the series of compounds, and the fact that X-ray crystal structures of organocobaloximes clearly reveal important effects of steric bulk of one axial ligand on the structural properties at the *trans* axial ligand position [19]. We consequently attempted to improve this correlation, as well as to extend it to include the omitted compounds, by use of the modified Taft equation [10, 20] including the steric parameter, E_s . Using the extensive compilation of steric parameters of Unger and Hansch [21], E_s values were available for the organic ligand for 18 of the 24 compounds. Unfortunately, two-parameter correlations of T_1 including the steric parameter, were all significantly

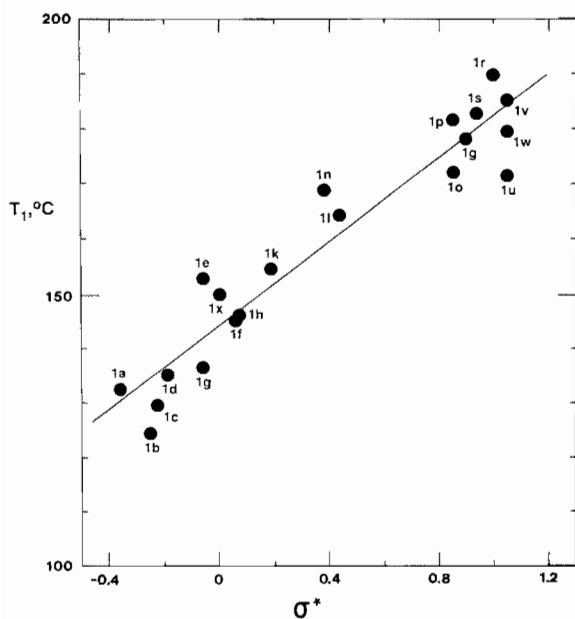


Fig. 4. Plot of the T_1 value (average of DSC and TGA determinations) of the alkyl(aquo)cobaloximes vs. σ^* , the Taft polar substituent constant. The solid line is a least squares line, $N = 20$, slope = 38.3 ± 2.9 °C, intercept = 144.1 ± 1.8 °C, $r^2 = 0.91$.

worse than the one-parameter correlation shown in Fig. 4. This may, however, be due to the inappropriateness of the usual E_s steric parameters for use with octahedral organometallic compounds.

Somewhat surprisingly, T_1 failed to correlate with the value of the pK_a for proton dissociation from the axial water ligand (eqn. (1)) [17, 18, 22, 23]. As this pK_a clearly reflects



the strength of the interaction of the axial water ligand with the cobalt atom, such a correlation might be anticipated. Similarly, ΔH_1 the enthalpy associated with axial water loss also failed to correlate with pK_a (eqn. (1)) as well as with σ^* , and addition of the steric parameter, E_s , failed to improve the latter correlation. Similarly, ΔH_1 failed to correlate with T_1 except for the four aromatic compounds for which a strong, linear correlation with a large positive slope was found. T_2 (loss of the organic ligand) also failed to correlate with σ^* and addition of the steric parameter did not improve the situation. However, there appears a tendency for T_2 to decrease with increasing chain length of the R group. This trend parallels that observed by previous authors for Co(salen)L² complexes (L² = 2,4-alkanedionate ligand) [5] and for the RCo(salen)py system [4].

In another attempt to account for anticipated steric effects, the compounds were grouped according to structure, into three categories: substituted methylcobaloximes (R = CH₃, (CH₃)₃SiCH₂, (CH₃-CH₂)₂CH, (CH₃)₂CH, ICH₂, CF₃CH₂, ClCH₂, CH₃OOCCH₂, and CH₃CH₂OOCCH₂), substituted ethylcobaloximes and arylcobaloximes. Within the series of nine substituted methyl compounds the correlation of T_1 with σ^* ($r^2 = 0.92$) was not significantly improved over that for all of the compounds (Fig. 4). However, a very good correlation ($r^2 = 0.96$) was found for T_1 with pK_a (eqn. (1)) for eight of the nine compounds (omitting R = (CH₃)₃SiCH₂, Fig. 5). The negative slope of this correlation is as anticipated, indicating that the loss of axial water becomes increasingly facile as the strength of interaction between the axial water ligand and the cobalt center declines. Within this series of substituted methyl compounds, ΔH_1 was essentially invariant (57 ± 3 kJ/mol), and no correlations with T_2 could be found. Unfortunately, the utility of grouping the compounds structurally does not extend past the substituted methyl compounds as no correlations could be found among the substituted ethylcobaloximes, and none of the thermal parameters of the arylcobaloximes correlated significantly with the Hammett σ_p or σ_m constants [20].

We have also searched, with some success, for correlations of thermal parameters involving axial water loss (*i.e.*, T_1 and ΔH_1) with solution kinetics of

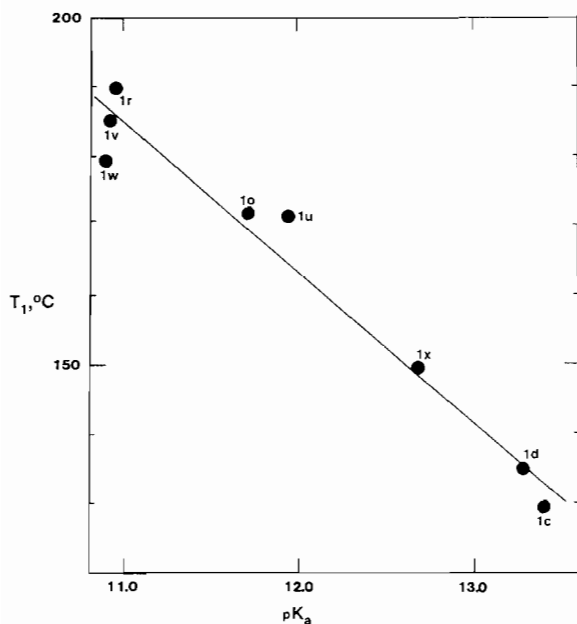


Fig. 5. Plot of the T_1 value (average of DSC and TGA determinations) for eight substituted methyl(aquo)cobaloximes vs. the pK_a for proton dissociation from the axial water ligand. The solid line is a least squares fit, $N = 8$, slope = -21.8 ± 1.8 °C, intercept = 424.6 ± 21.8 °C, $r^2 = 0.96$.

axial ligand exchange processes of organocobaloximes. Since such axial ligand exchange processes are known to be dissociatively dominated [17, 18, 24–27], the energetics of such processes must be expected to be related to the strength of the axial ligand bond. Thus, T_1 for nine (of 12 compounds for which data were available) was found to correlate well ($r^2 = 0.95$) with the logarithm of the rate constant for substitution of axial water by pyridine ($\log k_{\text{on}}^{\text{py}}$) at 25.0 °C, ionic strength 1.0 M [17] (Fig. 6b) and with the logarithm of the rate constant for the reverse process ($\log k_{\text{off}}^{\text{py}}$, $r^2 = 0.92$) for 10 of 12 compounds for which data were available (Fig. 6a). However, ΔH_1 failed to correlate with either of these variables. As the correlations in Fig. 6 span at least four and one-half orders of magnitude in reactivity, they seem quite significant. In both cases, kinetic lability is associated with greater ease of axial water loss (*i.e.*, lower T_1). Similar, although slightly less significant correlations were found for T_1 with solution kinetic parameters for ligand substitution by a primary amine ligand [18].

There is a substantial amount of literature data available on the solid state structures of organocobaloximes from X-ray crystallography studies [19]. Such solid state structural data should be expected to have direct bearing to the solid state thermal processes considered in this study. Unfortunately, little X-ray crystal data is available for alkyl(aquo)cobaloximes, but numerous structures have been

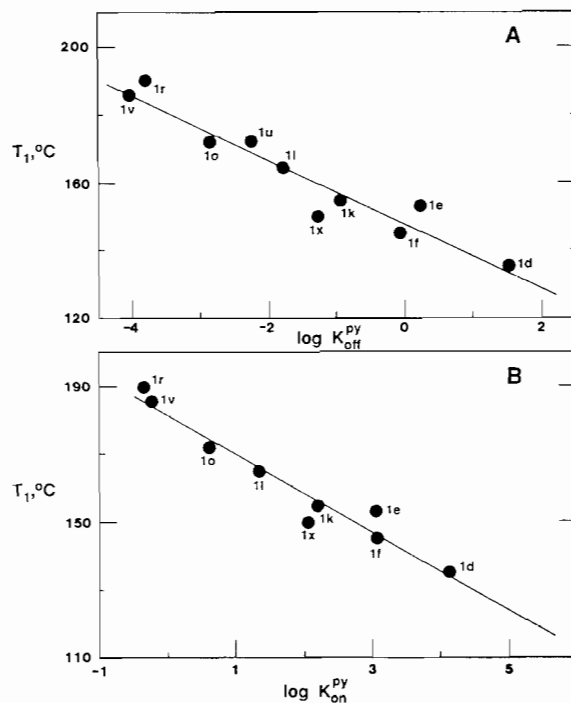


Fig. 6. Plots of the T_1 value (average of DSC and TGA determinations) vs. $\log k_{\text{off}}^{\text{py}}$, the rate constant for pyridine dissociation from the corresponding alkyl(pyridine)cobaloxime (a); vs. $\log k_{\text{on}}^{\text{py}}$, the rate constant for axial ligation of pyridine (b). The rate constants refer to 25 °C and 1.0 M ionic strength. Solid lines in (a) and (b) are least squares fitted with slopes of -11.5 ± 1.0 °C and -9.5 ± 1.0 °C and intercepts of 181 ± 2 °C and 147 ± 2 °C respectively. The respective correlation coefficients (r^2) were 0.95 and 0.92 respectively.

determined for alkyl(pyridine)cobaloximes [19]. If we assume that structural parameters, such as axial bond lengths, in the $\text{RCo}(\text{D}_2\text{H}_2)\text{py}$ series should parallel those in the $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ series, relationships between the structural properties of the former with the thermal properties of the latter seem likely. Indeed, a fairly good correlation ($r^2 = 0.92$) for the T_1 of $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ with the axial Co–N bond length ($2.039\text{--}2.099$ Å) of the analogous $\text{RCo}(\text{D}_2\text{H}_2)\text{py}$ was found for the six compounds for which data was available. The slope of this correlation was strongly negative (-930 °C/Å) displaying the expected strong dependence of axial ligand bond strength with bond length. However, no other correlations between thermal and structural properties could be found, *i.e.* T_1 did not correlate with the axial Co–C bond length, and neither ΔH_1 nor T_2 correlated with either axial ligand bond length.

The above observations suggest that for an extensive compound series (such as the present one) which encompasses wide variations in the nature of the R group, kinetic rather than thermodynamic factors are a better measure of the axial bond stability. This

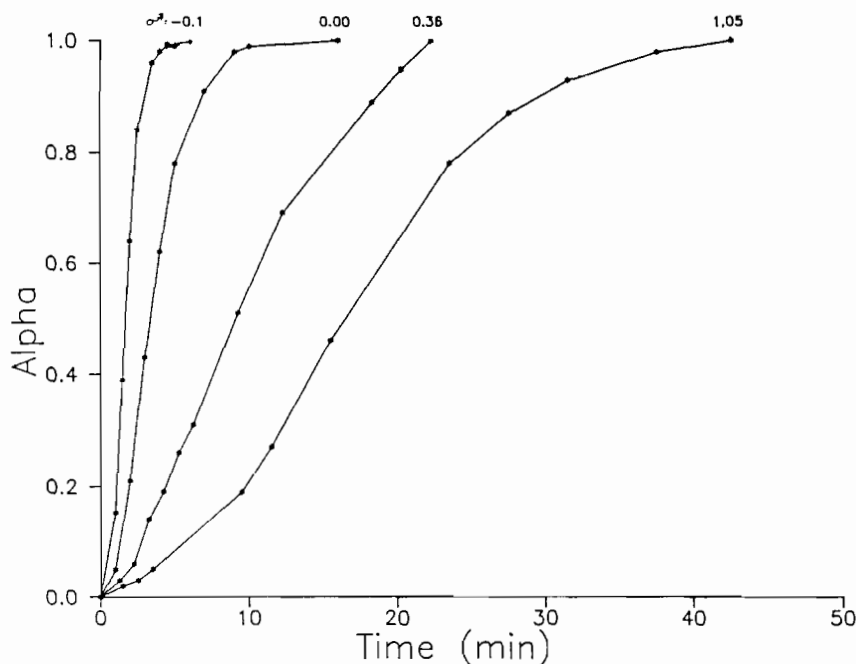


Fig. 7. Isothermal ($T_{\text{iso}} = 131.0 \pm 1.5$ °C) TGA weight loss curves for $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$. R is CH_3CH_2 , CH_3 , $\text{CH}_3\text{CH}=\text{CH}-$, and ClCH_2 from left to right. The σ^* parameter is shown for each compound.

is supported by: (a) the absence of significant correlations involving ΔH values for the various transitions when taken across the entire compound series, and (b) the good correlation that is observed between T_1 and ΔH_1 when a set of compounds with very similar R (e.g., aromatic) groups are chosen (*vide supra*). Shifts in characteristic DSC or TGA temperatures signal changes in thermolysis kinetics. Figure 7 illustrates isothermal TGA scans for selected compounds in the $\text{RCo}(\text{DH})_2\text{OH}_2$ series for the transition regime corresponding to T_1 in the dynamic heating case. The shift in reaction rate is in the expected direction, *i.e.* deaquation is more facile when the R group is less electron-withdrawing. Rate constants are accessible through analysis of data such as those shown in Fig. 7. However, contrary to previous practice [3–7], we have not attempted to utilize these parameters for our correlations. The point to emphasize here is that T_1 is a convenient measure of the deaquation (or depyridination) rate constant, and extraction of this parameter does not involve difficulties associated with dubious model assumptions or tedious data analyses.

Thermal data has also been collected for a somewhat more limited series of alkyl(pyridine)cobaloximes (Table III). Of the 19 compounds studied only four showed three clear transitions (see, e.g., Fig. 8a and b) while most of the remainder showed two transitions. Two of the compounds

(R = $p\text{-CH}_3\text{CC}_6\text{H}_4$ and $p\text{-CF}_3\text{C}_6\text{H}_4$) decomposed completely in a concerted manner showing only a single transition near 300 °C (see, e.g., Fig. 9a and b). It is reasonably clear that for those compounds showing three transitions, the transitions may be assigned to the same three processes as before, *i.e.* loss of the axial pyridine ligand (T_1), loss of the axial organic ligand (T_2) and decomposition of the 'core' complex (T_3). These assignments are supported by the fact that for R = $(\text{CH}_3\text{CH}_2)_2\text{CH}$ the weight loss for the T_1 process was 111% of the value calculated for loss of axial pyridine, while the weight loss accompanying the T_2 process was 100% of that calculated for loss of the organic ligand (as RH). Furthermore, the average T_3 values (DSC, $N = 19$, $T_3 = 292 \pm 6$ °C; TGA, $N = 4$, $T_3 = 279 \pm 15$ °C) are in excellent agreement with those obtained for T_3 for the $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ series. For those compounds showing only two transitions, the first transition (*i.e.*, T_{overlap} in Table III) may again be assumed to represent the simultaneous loss of both axial ligands since the average temperature for the upper transition (DSC, $N = 13$, $T_3 = 291 \pm 5$ °C) agreed excellently with that for the four compounds showing three transitions (DSC, $T_3 = 290 \pm 7$ °C) as well as with the average T_3 value for the $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ series. Once again the weight loss accompanying the overlap

TABLE III. DSC and TGA Data for Alkyl(pyridine)cobaloximes, $\text{RCo}(\text{D}_2\text{H}_2)\text{Py}$

Compound	R	T_1 (°C) DSC(TGA)	T_{overlap} (°C) DSC(TGA)	Weight loss ^a	T_2 (°C) DSC(TGA)	T_3 (°C) DSC(TGA)	ΔH_3^f (kJ/mol)
2b	$\text{CH}_3(\text{CH}_2)_5$		208(214)	122		291(264)	
2c	$(\text{CH}_3\text{CH}_2)_2\text{CH}$	113(131) ^{b, g}			181(134) ^{c, g}	283	
2e	CH_3CH_2		196(208)	133		289	
2h	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2$		212(226)	123		289	
2i	HOCH_2CH_2		185(198)	114		287	
2k	$\text{CH}_3\text{OCH}_2\text{CH}_2$		198(222)	132		288	-331
2p	<i>m</i> - $\text{CH}_3\text{OOC}_6\text{H}_4$		250(225)	109		300	
2r	CF_3CH_2		235(251)	- ^e		293	-346
2s	<i>p</i> - $\text{CH}_3\text{COC}_6\text{H}_4$ ^d					301	
2t	<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$					307(296)	
2v	$\text{CH}_3\text{OOCCH}_2$	137			178	295	
2y	HOOCCH_2		235			292	
2z	<i>p</i> - FC_6H_4	214(222)				297(288)	
2aa	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2$		162(172)	121		284	-349
2bb	CH_3		246(250)	- ^e		289	-396
2cc	$\text{C}_6\text{H}_5\text{CH}_2$		205(204)	103		399(271)	-318
2dd	$\text{HOOCCH}_2\text{CH}_2$		212			294	
2ee	$\text{CH}_3\text{OOCCH}_2\text{CH}_2$		213			289	
2ff	$\text{HOOCCH}(\text{CH}_3)$	165			186	286	-380

^aWeight loss expressed as percentage of the value calculated for loss of both axial pyridine and the organic ligand as RH. ^bWeight loss (as percentage of value calculated for loss of axial pyridine) was 111%. ^cWeight loss (as percentage of value calculated for loss of RH) was 100%. ^dOnly a single transition was observed. ^eWeight loss plateaux not clearly resolved. ^fEnthalpies are presented only in those cases where the transitions are clearly resolved. Exothermic cases are denoted by a negative sign. ^g $\Delta H_1 = 14$ kJ/mol, and $\Delta H_2 = 18$ kJ/mol for T_1 and T_2 transitions respectively.

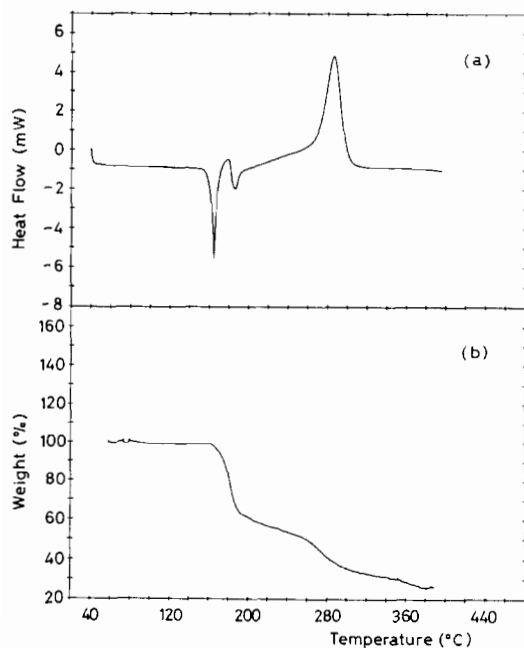


Fig. 8. DSC (a) and TGA (b) traces for an alkyl(pyridine)-cobaloxime [$\text{RCo}(\text{D}_2\text{H}_2)\text{py}$] sample [$\text{R} = \text{HOOCCH}(\text{CH}_3)$], exemplifying overlapped T_1 and T_2 transition regimes.

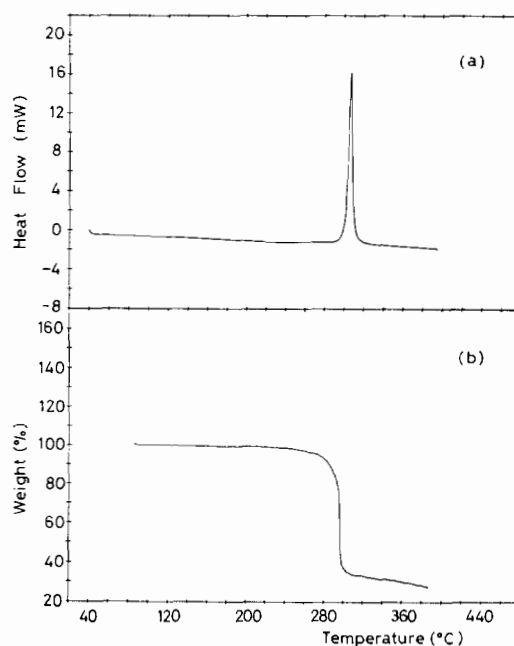


Fig. 9. DSC (a) and TGA (b) traces for $\text{RCo}(\text{D}_2\text{H}_2)\text{py}$ ($\text{R} = \text{CF}_3\text{C}_6\text{H}_4$) illustrating a case where all three transition regimes are overlapped.

transition was significantly greater than that calculated for the combined loss of pyridine and the organic ligand as RH ($N = 8$, $120 \pm 10\%$). However, again these values showed a tendency to increase with increasing T_{overlap} , suggesting some volatility of the $\text{RCo}(\text{D}_2\text{H}_2)$ moiety as also found in the aquo complexes.

Although the 13 complexes showing the overlap behavior showed a clear trend for T_{overlap} to increase with increasing σ^* of the organic ligand, the correlation (omitting two outlying compounds, $\text{R} = \text{CH}_3$ and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2$) was much worse than that for T_1 versus σ^* for the $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ series ($N = 13$, $r^2 = 0.68$). Also, although T_{overlap} showed a trend to increase with increasing T_1 for the analogous $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ compounds, no significant correlation was found. However, some excellent correlations (not shown) were obtained for T_{overlap} for the $\text{RCo}(\text{D}_2\text{H}_2)\text{py}$ compounds with solution kinetic parameters for axial ligand substitution. For instance, T_{overlap} for 5 of 6 compounds (omitting $\text{R} = \text{CH}_3$) for which data were available correlated very strongly with $\log k_{\text{on}}^{\text{py}}$ (for ligation of axial pyridine to the appropriate $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$, $r^2 = 0.95$) and with $\log k_{\text{off}}^{\text{py}}$ (for pyridine dissociation, $r^2 = 0.94$) [17]. In both cases the slope of the correlation was negative, as anticipated, due to the dissociative nature of the ligand substitution processes. Similarly, excellent correlations for four of five compounds (again omitting $\text{R} = \text{CH}_3$) for which data were available were found for T_{overlap} with logarithm of the rate constant for axial ligation of dimethoxyethylamine to the appropriate $\text{RCo}(\text{D}_2\text{H}_2)\text{OH}_2$ ($r^2 = 0.99$) and with the logarithm of the rate constant for the reverse process ($r^2 = 0.99$).

Unfortunately, X-ray crystal structures are available for only three of the $\text{RCo}(\text{D}_2\text{H}_2)\text{py}$ compounds in our series. However, the T_{overlap} values for these three compounds were virtually colinear with the carbon-cobalt bond distance, T_{overlap} increasing about 45°C for an 0.065 \AA shortening of the $\text{Co}-\text{C}$ bond, but no such trend existed for T_{overlap} and the axial $\text{Co}-\text{N}$ bond distance.

Acknowledgements

This research was supported by the Robert A. Welch Foundation, Houston, Tex. (Grant #Y-749 to K.L.B.) and by the DuPont Company (K.R.).

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