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COBALT-PYRIDINE BOND STRENGTH IN RCo[*N,N′*-ETHYLENEBIS(SALICYCLIDENEAMINATO)] (PYRIDINE) R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu

*C. T. Mortimer** and *Jan M. B. Steele*

CHEMISTRY DEPARTMENT, UNIVERSITY OF KEELE,
KEELE, STAFFORDSHIRE, ST5 5BG, U.K.

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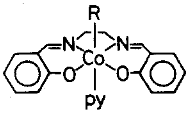
The use of differential scanning calorimetry has provided enthalpies, ΔH (298 K), of the dissociation reactions

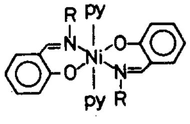
$$\mathrm{RCo(salen)(pyridine)(c)} \rightarrow \mathrm{RCo(salen)(c)} + \mathrm{pyridine(g)}$$

R = Me 34.5, Et 21.9, *n*-Pr 12.8, *i*-Pr 11.1, *n*-Bu 8.3 and *i*-Bu 13.5 kJ mol^{-1}

Miyokawa, Kawarada and Masuda [1] have prepared the compounds pyridine[*N,N′*-ethylenebis(salicylideneaminato)]alkylcobalt(III), RCo(salen)(py), R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu). They have used thermal analysis to study the kinetics of pyridine dissociation and have found an approximately linear relationship between the rate constant log k (400 K), and the inductive substituent constants for R. The more electron donating R groups, e.g. *i*-Pr, labilize the bond trans to it between cobalt and pyridine. Thus, the log k (400 K) values, which represent the kinetic stability of the Co(III)-py bonding, increase in the following order of R, such that the methyl compound is the most stable and the *i*-Pr compound is the least stable; Me < Et < *i*-Bu < *n*-Pr < *n*-Bu < *i*-Pr.



RCo(salen)(py)



Ni(salam)$_2$(py)$_2$

The question arises, to what extent is this kinetic trans effect reflected in a weakening of the Co(III)-py bond in the ground state molecule as R is changed? To

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* To whom correspondence should be addressed.

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answer this question, we have used differential scanning calorimetry to measure the enthalpies of the dissociation of pyridine, reaction (1).

$$\mathrm{RCo(salen)(py)(c)} \rightarrow \mathrm{RCo(salen)(c)} + \mathrm{py(g)} \qquad (1)$$

In so far as the enthalpies of sublimation of RCo(salen)(py) and RCo(salen) can be regarded as the same, we may equate the enthalpies of these reactions to the bond dissociation enthalpies D(Co-py).

Experimental

The pyridine complexes, RCo(salen)(py), were isolated by crystallization of the corresponding aquo complexes from a pyridine-methanol (1 : 3) solution [1]. The C, H and N analyses were satisfactory. The aquo complexes were prepared by the literature method [2] from salicyclaldehyde, ethylenediamine and $CoCl_2 \cdot 6H_2O$ to obtain a solution of cobalt(salen). The R group was introduced from the corresponding alkyl iodide.

Thermal data were obtained by use of the Perkin–Elmer DSC 1A. Nitrogen flowed over the sample. Details are shown in Table 1. The values of $\Delta H(T_p/\mathrm{K})$ refer to the peak temperatures T_p of the depyridination reaction (1). Observed percentage weight losses were close to the calculated values, except for the compound R = *i*-Bu, where the difference is 0.5%. Possibly, additional decomposition occurs with this compound.

In order to calculate the enthalpies, ΔH (298 K) of reaction (1) at 298 K, the values of $\Delta H(T_p/\mathrm{K})$ must be corrected for the enthalpy changes which result from heat capacity effects.

$$\Delta H(298\ \mathrm{K}) = \Delta H(T_p/\mathrm{K}) + \int_{298}^{T_p/K} \{C_p[\mathrm{RCo(salen)(py)}]\,\mathrm{d}t - C_p[\mathrm{RCo(salen)}]\,\mathrm{d}t - $$
$$- C_p(\mathrm{py})\,\mathrm{d}t\}$$

Table 1 Thermal data for RCo(salen)(py)

R	T_p, K	Wt. loss, %		$\Delta H(T_p/\mathrm{K})$, kJ mol^{-1}	$\Delta H(C_p$, Co), kJ mol^{-1}	ΔH(298 K), kJ mol^{-1}
		obs.	calc.			
Me	480	18.87	18.86	15.8	18.7	34.5
Et	455	18.38	18.25	6.3	15.6	21.9
n-Pr	387	17.17	17.68	5.4	7.9	13.3
i-Pr	389	17.48	17.68	2.8	8.2	10.0
n-Bu	359	17.02	17.14	3.1	5.3	8.4
i-Bu	364	16.61	17.14	7.7	5.6	13.3

The difference, $\Delta H(C_p, \mathrm{Co})$, between the first two C_p terms can be derived simply by calculating ΔH from the area of the DSC curve between the two base lines when the pan contains RCo(salen)(py) and RCo(salen), respectively. Unfortunately, the lack of reproducibility of the base line with the earliest and now ageing model 1A of the Perkin–Elmer differential scanning calorimeter made it difficult to quantify this difference, so that we have had to assume it to be zero. the correction, $\Delta H(C_p, \mathrm{py})$, due to the heat capacity of gaseous pyridine can be calculated by using the following relationship [3], which refers

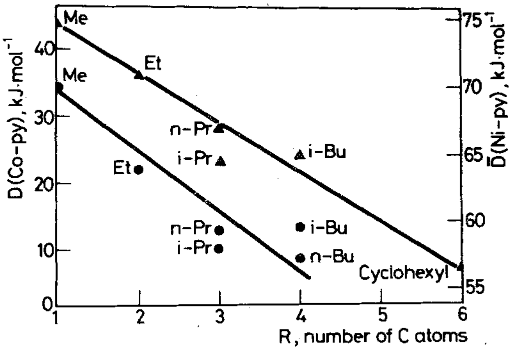
$$C_p(\text{pyridine})/\text{J mol}^{-1}\,\text{deg}^{-1} = -34.57 + 44.38 \times 10^{-2}\, T/\text{K} - 22.87 \times 10^{-5}\, (T/\text{K})^2$$

to the temperature range 374–500 K. We assume that this equation also refers to gaseous pyridine in the temperature range 298–374 K.

The enthalpies of dissociation, $\Delta H(298\ \mathrm{K}) = \mathrm{D(Co\text{-}py)}$, decrease in the following order, which is the same as that found for the $\log k$ (400 K) values,

$$\mathrm{Me} > \mathrm{Et} > i\text{-}\mathrm{Bu} > n\text{-}\mathrm{Pr} > i\text{-}\mathrm{Pr} > n\text{-}\mathrm{Bu}$$

except for *i*-Pr and *n*-Bu, the positions of which are inverted. There is an almost linear relationship, shown in the Figure, between $\Delta H(298\ \mathrm{K}) = \mathrm{D(Co\text{-}py)}$ and the number of carbon atoms in the R groups for R = Me, Et, *n*-Pr and *n*-Bu. A similar relationship has been found for the enthalpies of dissociation, $\Delta H(298\ \mathrm{K})$, of pyridine from bis(pyridine)bis(*N*-alkyl-substituted-salicyclideneaminato)nickel(II), $\mathrm{Ni(salam)_2(py)_2}$, reaction (2), although it should



$$\mathrm{Ni(salam)_2(py)_2(c)} \rightarrow \mathrm{Ni(salam)_2(c)} + 2\mathrm{py(g)} \ldots \qquad (2)$$

be noted that the alkyl group is bonded to the chelating ligand rather than directly to the metal. The following values of $\frac{1}{2}\Delta H(T_p/\mathrm{K})$, T_p/K [4], $\frac{1}{2}\Delta H(C_p)$, and $\frac{1}{2}\Delta H(298\ \mathrm{K})$ are used; R = Me 65.0, 406, 10.0, 75 ± 1; Et 62.5, 392, 8.5, 71 ± 3; *n*-Pr

58.0, 398, 9.1, 67 ± 1; *i*-Pr 55.0, 402, 9.5, 64.5 ± 1; *i*-Bu 56.0, 397, 9.0, 65 ± 1; and cyclohexyl 49.0, 383, 7.5, 56.5 ± 1 kJ mol^{-1}. It is seen that the values of $\bar{D}$(Ni-py), for a given R group, are much greater than for D(Co-py) in RCo(salen)(py), where the oxidation state of cobalt is + 3, but that the slope of the line for RCo(salen)(py) is more than twice that of the line for D(Ni-py) (note the different ordinate scale in the two cases).

References

1 K. Miyokawa, T. Kawarada and I. Masuda, Thermochim. Acta, 83 (1985) 235.

2 G. N. Schrauzer, J. W. Sibert and R. J. Windgassen, J. Amer. Chem. Soc., 90 (1968) 6681.

3 J. P. McCullough, D. R. Douslin, J. F. Messely, I. A. Hossenlopp, T. C. Kincheloe and G. Waddington, J. Amer. Chem. Soc., 79 (1957) 4289.

4 H. Masuda, T. Kawarada, K. Miyokawa and I. Masuda, Thermochim. Acta, 63 (1983) 307.

Zusammenfassung — Mit Hilfe der Differential-Scanning-Kalorimetrie wurden die Enthalpien ΔH(298 K) der Dissoziationsreaktionen RCo(salen)(Pyridin)(c) → RCo(saleo)(c) + Pyridin(g) bestimmt: R = Me 34,5, Et 21,9, *n*-Pr 12,8, *i*-Pr 11,1, *n*-Bu 8,3 und *i*-Bu 13,5 kJ·mol^{-1}.

Резюме — Использование дифференциальной сканирующей калориметрии представило возможность определения энтальпий ΔH(298 K) реакций диссоциации комплекса по следующей схеме:

RCo(сален)(пиридин) → RCo(сален) + пиридин(г)

Величины энтальпий для комплекса с различными радикалами R были равными в случае R = метил — 34,5; этил — 21,9; н-пропил — 12,8; изопропил — 11,1; н-бутил — 8,3 и изобутил — 13,5 кдж·моль$^{-1}$.