

THERMAL DECOMPOSITION OF DERIVATIVES
OF ORGANOCOBALT (III)
[RCo^{III}(bae)] and [RCo^{III}(bae)]H₂O]

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ABSTRACT: Thermal stability and thermal decomposition of organocobalt (III) complexes like [RCo^{III}(bae)] and [RCo^{III}(bae)]H₂O], where bae = bis (acetylacetonone) ethylenediamine and R = CH₃, C₂H₅, n-C₃H₇, i-C₃H₇, n-C₄H₉, i-C₄H₉, s-C₄H₉, c-C₆H₁₁CH₂, c-C₆H₁₁ and C₆H₅CH₂ (or φ CH₂), were studied by differential thermal analysis (DTA) and conventional chemical analysis.

KEY-WORDS: Derivatives of organocobalt (III); thermal decomposition.

INTRODUCTION

Recently, organocobalt (III) compounds containing equatorial ligands with a delocalized electronic structure were prepared and their electrochemical behaviour were studied by CHUM *et alii*^{1,2}, BENEDETTI *et alii*³⁻⁵ and QUINTALE Jr. *et alii*⁶. For all compounds, the rupture of Co-C bond has been considered as the first step in the electrochemical oxidation.

Little information exists in the literature concerning the thermal behavior of these compounds⁷⁻⁹, mainly about [RCo^{III}(bae)] derivatives.

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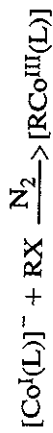
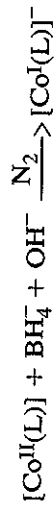
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This work has the purpose to contribute to the knowledge of the thermal stability, especially of the Co-C bond, of organocobalt (III) derivatives. So, the thermal behaviour of complexes of the type $[\text{RCo}^{\text{III}}(\text{bae})]$, where bae = bis (acetylacetonate) ethylenediamine and $\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $i\text{-C}_4\text{H}_9$, $c\text{-C}_6\text{H}_{11}\text{CH}_2$ and of the type $[\text{RCo}^{\text{III}}(\text{bae})\text{H}_2\text{O}]$, where $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $i\text{-C}_3\text{H}_7$, $c\text{-C}_6\text{H}_{11}\text{CH}_2$, $c\text{-C}_6\text{H}_{11}$ and $\text{C}_6\text{H}_5\text{CH}_2$ (or ϕCH_2) was studied mainly by differential thermal analysis (DTA).

EXPERIMENTAL

Organocobalt (III) derivatives were prepared following the procedure described by SCHRAUZER¹⁰, according to the reactions:



Nickel chloride was used as catalyser and the compounds were purified in methanol or chloroform to produce hexacoordinated or pentacoordinated derivatives, respectively.

Differential Thermal Analysis (DTA)

DTA curves, to a maximum of 1 100°C, were obtained as early described by MARQUES LUIZ *et alii*¹¹ by heating at a rate of 8.9°C min⁻¹ in air at atmospheric pressure. α -Alumina, previously calcinated at 1 150°C was used as a reference material and the samples were diluted in it at 3% (m/m).

RESULTS AND DISCUSSION

The thermal decomposition of all complexes studied, as well as the kinetics of decomposition, follow characteristic pathways, depending on the nature of the ligands.

In Figure 1, the DTA curves for all anhydrous complexes show a breadth exothermic peak at the end of each curve, suggesting a slow and consecutive thermal decomposition process. This figure also shows that the exothermic peak begins around 90°C (except for the $s\text{-C}_4\text{H}_9$ that begins at 330°C) and that the final

decomposition temperature depends on the nature of the R group: $c\text{-C}_6\text{H}_{11}\text{CH}_2$ (440°C); $n\text{-C}_3\text{H}_7$ (450°C); $s\text{-C}_4\text{H}_9$ (480°C); C_2H_5 (510°C); $n\text{-C}_4\text{H}_9$ (530°C); $i\text{-C}_4\text{H}_9$ (560°C) and $i\text{-C}_3\text{H}_7$ (660°C). For compounds with $\text{R} = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$ and $n\text{-C}_4\text{H}_9$, the thermal decomposition mechanism seems to be similar, but for the others it seems to be different to each one.

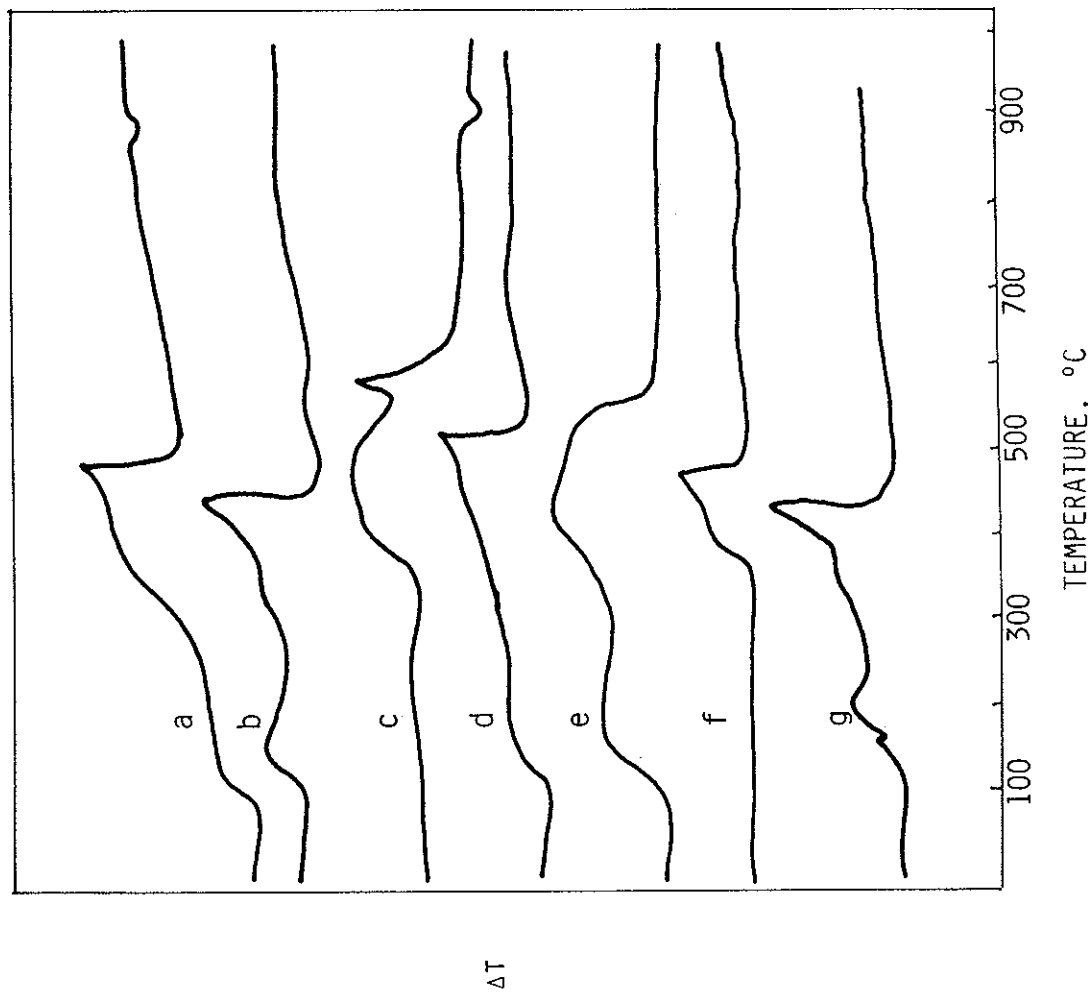


Figure 1 - DTA curves for $[\text{RCo}^{\text{III}}(\text{bae})]$ complexes diluted in α -alumina at 3% (m/m). Heating rate: 8.9°C min⁻¹ and sweep rate: 15cm h⁻¹. R groups are: (a) C_2H_5 ; (b) $n\text{-C}_3\text{H}_7$; (c) $i\text{-C}_3\text{H}_7$; (d) $n\text{-C}_4\text{H}_9$; (e) $i\text{-C}_4\text{H}_9$; (f) $s\text{-C}_4\text{H}_9$; and (g) $c\text{-C}_6\text{H}_{11}\text{CH}_2$.

For all compounds, the first step of thermal decomposition probably occurs with the loss of the R group, followed by the decomposition of the ligand *bae* and finally, by the formation of the cobalt oxide, Co_3O_4 , in accordance with the mechanism proposed by BENEDETTI *et alii*⁸ for analogous compounds. The nitrogens from the equatorial ligand are lost as HNO_2 as verified by testing with sulfanilic acid and α -naphthylamine.

The analysis of DTA curves also suggests that the thermal decomposition mechanism is more influenced by the type of carbon bonded to the cobalt atom than by the number of carbons in the R group.

Figure 2 shows the DTA curves for hexacoordinated compounds. The first weight loss, an endothermic peak, occurs between 100 and 180°C and is attributed to the elimination of the water coordinated to the cobalt atom. The exothermic peaks correspond to the thermal decomposition of the rest of the cobalt complex.

From the DTA curves of figures 1 and 2 it is clear that the water coordinated changes the thermal stability of the compounds, suggesting that the decomposition mechanism also changes. But, even in the hexacoordinated complexes the nature of the R group plays an important role in their thermal decomposition.

The endothermic peak for $[\text{RCo}^{\text{III}}(\text{bae})]$ with $\text{R} = \text{C}_2\text{H}_5$ and $i\text{-C}_3\text{H}_7$, and for $[\text{RCo}^{\text{III}}(\text{bae})\text{H}_2\text{O}]$ with $\text{R} = \text{CH}_3$ and C_2H_5 observed at 890, 900, 700 and 710°C, respectively, can be assigned to the reduction of Co_2O_3 to Co_3O_4 . Although the final product of the thermal decomposition is Co_3O_4 , this endothermic peak was not observed for the other compounds.

CONCLUSION

DTA curves allowed to verify that the thermal decomposition of these compounds occurs by a slow and consecutive process. Water coordinated at the sixth coordination position increases the thermal stability and changes the thermal decomposition mechanism.

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MERCADANTE, A. *et alii* - Termodecomposição de derivados de organocobalto (III): $[\text{RCo}^{\text{III}}(\text{bae})]$ e $[\text{RCo}^{\text{III}}(\text{bae})\text{H}_2\text{O}]$. *Ecl. Quím.*, São Paulo, **14**: 21-26, 1989.

*RESUMO: Através da análise térmica diferencial, estudou-se a estabilidade térmica e a termodecomposição de derivados de organocobalto (III): $[\text{RCo}^{\text{III}}(\text{bae})]$ e $[\text{RCo}^{\text{III}}(\text{bae})\text{H}_2\text{O}]$, onde *bae* = bis (acetilacetona) etilenodimina; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_5$ e $\text{C}_6\text{H}_5\text{CH}_2$ (ou ϕCH_2).*

UNITERMOS: Derivados de organocobalto (III); termodecomposição.

Ecl. Quím., São Paulo, **14**: 21-26, 1989.

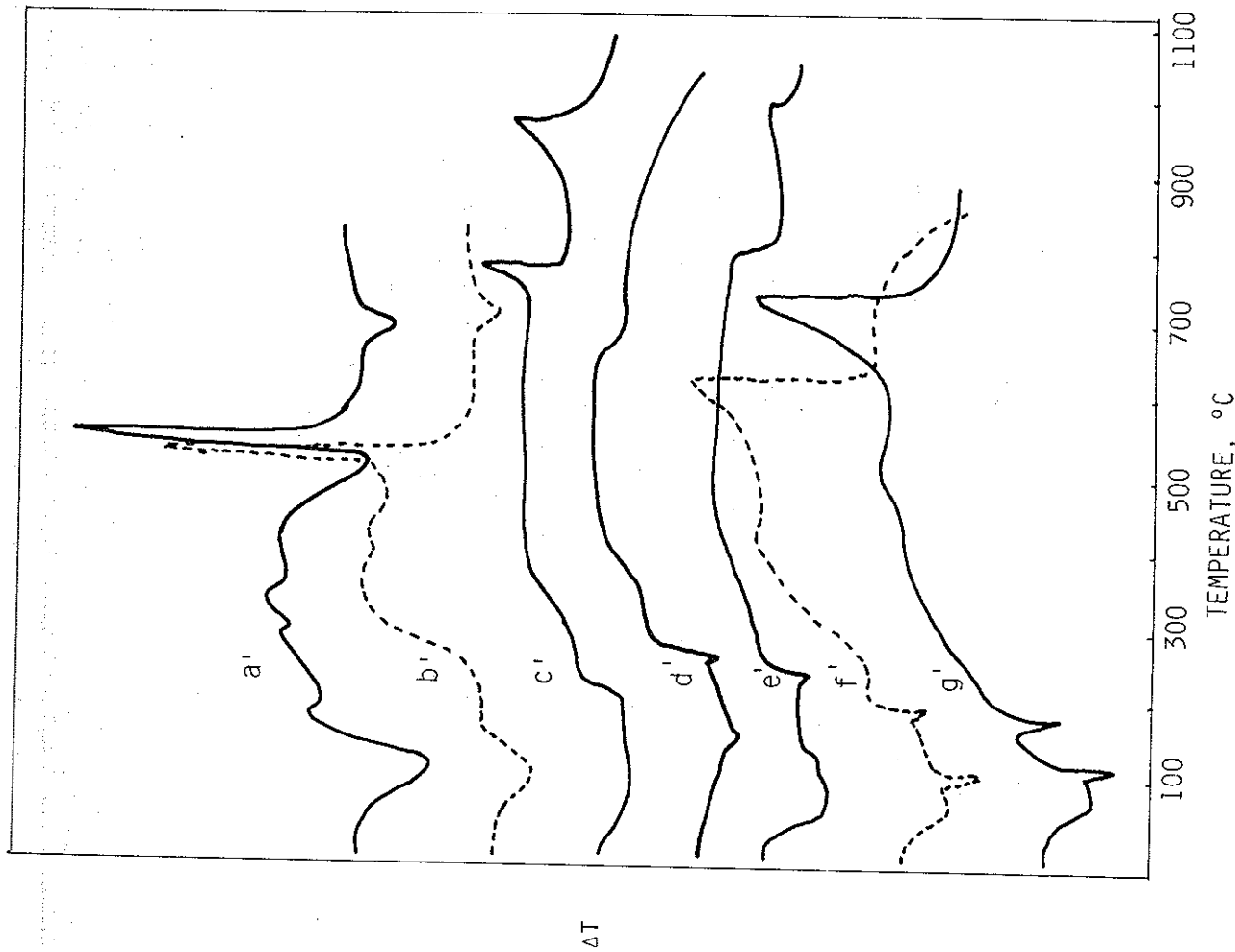


Figure 2 - DTA curves for $[\text{RCo}^{\text{III}}(\text{bae})\text{H}_2\text{O}]$ derivatives diluted in α -alumina at 3% (m/m). Heating rate: $8.9^\circ\text{C min}^{-1}$ and sweep rate: 15cm h^{-1} . R groups are: (a') CH_3 ; (b') C_2H_5 ; (c') $n\text{-C}_3\text{H}_7$; (d') $i\text{-C}_3\text{H}_7$; (e') $c\text{-C}_6\text{H}_{11}\text{CH}_2$; (f) $c\text{-C}_6\text{H}_{11}$; and (g') ϕCH_2 .

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