

THERMAL ANALYSIS OF PENTAFLUOROPHENYL ORGANO COMPLEXES OF COBALT(III) WITH SCHIFF BASES

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(Received November 29, 1976)

A series of complexes of the type $(C_6F_5)CoL_4B$ with tetradentate ligands ($L_4 =$ acacen (N,N'-ethylene-bis acetylacetonate dianion), mesalen (N,N'-ethylene-bis-7,7'-dimethylsalicylideneiminato dianion); $B = H_2O, NH_3, py, ba, pip, en$ and $L_4 = dotnH$ (diacetylmonoximeiminodiacetyl-monoximateiminopropane-1,3 monoanion), $B = Br, I, CN$) has been studied, using TG and DTA methods to obtain information concerning the decomposition mechanism and the influence of the ligands on the thermal stabilities of cobalt-carbon and cobalt-axial base bond.

The elimination of the axial base leads to the formation of pentacoordinate complexes $(C_6F_5)CoL_4$ (when $L_4 =$ acacen, mesalen) and their subsequent decomposition involves cobalt-carbon bond rupture to form CoL_4 . In contrast, the latter reaction occurs first when the tetradentate ligand is dotnH.

It has been observed that the stability of the cobalt-carbon bond is related to the nature of the equatorial ligands, and decreases in the order: mesalen > acacen > dotnH.

Many organometallic complexes of cobalt(III) with Schiff bases have been described, and numerous data concerning their preparation, structure and chemical behaviour are known [1, 2].

However, the thermal behaviour of this type of complex is almost unknown, because systematic thermal analysis has not been carried out and only qualitative observations have been described.

As regards the several organic substituents used, the π -acceptor capacity or the higher electronegativity of the group C_6F_5 leads to stabilization of the metal-carbon bond and the complexes containing this substituent can be more easily studied.

Following our work on organometallic complexes of the perfluoro organic group C_6F_5 , we have recently described [3-5] complexes of the type $(C_6F_5)CoL_4B$, L_4 being the tetradentate acacen and mesalen dianions or the dotnH monoanion, and B a Lewis base. These complexes are all octahedral, with the tetradentate ligand occupying the four equatorial positions and the base B and the C_6F_5 group situated in the two trans axial positions. They are particularly appropriate for the study of simple processes such as the breaking of the cobalt-carbon and the cobalt-axial base bonds, as the intermediate products are sufficiently stable to be observed.

Experimental

The complexes were prepared by methods described earlier [3–5].

TG, DTG and DTA measurements were carried out in a Netzsch apparatus, model 429, under the following experimental conditions: platinum/platinum-rhodium thermocouple, platinum holders, heating rate: 5 °/min, sample size: 50 mg (120 mg for kinetic study), reference material: preheated alumina, atmosphere: static air, oxygen (20 ml/min) or an inert atmosphere (N₂ 25 ml/min).

Intermediate decomposition products were isolated and identified by IR, melting point and analytical determinations.

Results

The thermal decomposition of the complexes (C₆F₅)CoL₄B takes place according to the equations

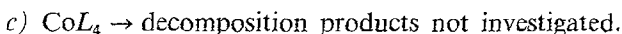
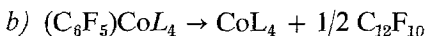
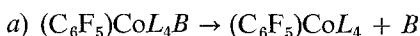


Table 1 shows the reactions and characteristic temperatures for each complex.

Table 1

Reactions and corresponding temperature ranges observed in thermal decomposition of (C₆F₅)Co(acacen) B. Inert atmosphere

Base B	a)		b)		c)	
	- B endothermic		- C ₆ F ₆ endothermic		Decomposition of Co(acacen)	
—			160	170		
H ₂ O	108	120	160	190		
NH ₃	100	110	160	190		
		a, +	b,		250	320
pyridine	160		180			
piperidine		120	180			
benzylamine		138	180			
ethylenediamine		170	180			

Complexes with acacen

When L₄ = acacen, the first step a) is only observed separately for complexes with B = H₂O and NH₃. In both cases the loss of the axial base occurs between 100 and 120°, producing the pentacoordinate complex, which is stable until

160°. Between 160 and 190° the breaking of the cobalt-carbon bonds takes place with formation of Co(acacen) and loss of the organic radical as $C_{12}F_{10}$, as shown in Fig. 1.

Finally, at 260° the decomposition of Co(acacen) takes place with progressive loss of weight being observed in an inert atmosphere; no compound of definite composition is formed, whereas Co_3O_4 is the final compound in the presence of air

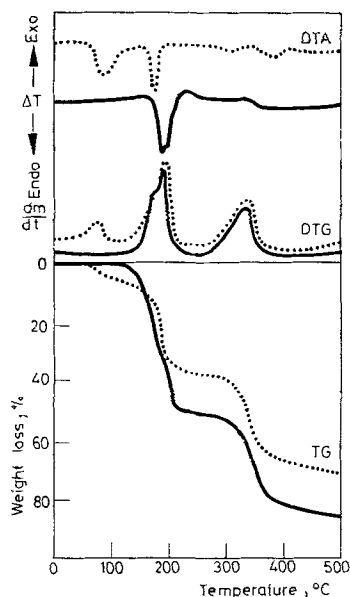


Fig. 1. Thermoanalytical curves of: $C_6F_5Co(acacen)py$ (full line) and $C_6F_5Co(acacen)H_2O$ (broken line) in nitrogen.

The complexes with $B =$ amine initially show a loss of weight corresponding to the elimination of the amine and the organic radical, demonstrating that processes *a*) and *b*) take place simultaneously. The two processes cannot be separated in the TG curve, but it is possible to conclude that elimination of the base occurs first, because intermediate products have different compositions, but do not contain the amine, as proved by analytical determinations. DTG and DTA curves show two peaks for most complexes. The pentacoordinate complex which was separately isolated exhibits a loss of weight corresponding to process *b*) only between 160 and 170°.

Complexes with mesalen

The thermal behaviour of the complexes with mesalen, viz. $(C_6F_5)Co(mesalen)$ $B(B = NH_3, py, pip)$ and $(C_6F_5)Co(mesalen)$, shows a similar pattern. The results are reported in Table 2. In this case processes *a*) and *b*) can be observed separa-

tely because elimination of the organic radical takes place at higher temperatures (between 240 and 260°). As can be observed in Table 2, elimination of the amine (process *a*) takes place between 110 and 190°, i.e. at temperatures higher than those observed in the corresponding complexes with acacen. This elimination leads to the formation of the pentacoordinate complex $(C_6F_5)_5Co(mesalen)$, which is stable until 240°, the cobalt-carbon bond then being broken to give the complex $Co(mesalen)$. This complex decomposes progressively in an inert atmosphere without yielding a product of definite composition even at 700°. However, it is quickly decomposed at 400° in an oxygen atmosphere, giving Co_3O_4 as the final product.

Table 2
Reactions and corresponding temperature ranges observed in thermal decomposition of $(C_6F_5)_5Co(mesalen)$ *B*

Base <i>B</i>	Medium	<i>a</i>)		<i>b</i>)		Nature of transformation	
		— Base		— C_6F_5		<i>a</i>)	<i>b</i>)
—	N_2			250	260	—	endo
—	O_2			250		—	exo
NH_3	O_2	125	160	240		endo	exo
pyridine	O_2	140	190	245		endo	exo
piperidine	O_2	110	120	242		endo	exo

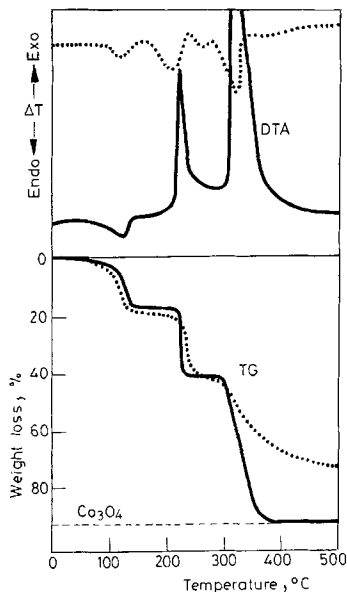


Fig. 2. TG and DTA curves of $C_6F_5Co(mesalen)py$; Full line: in oxygen; Broken line: in nitrogen.

The temperatures at which processes *a*) and *b*) take place are essentially the same in an inert atmosphere as in an oxygen atmosphere, which prevents overflow of the decomposition products out of the Pt sample holders.

All processes are endothermic in an inert atmosphere, while process *b*) is exothermic and process *a*) is highly exothermic in an oxygen atmosphere, corresponding to the combustion of the ligand to give Co_3O_4 (Fig. 2).

Complexes with dotnH

The TG curves of the complexes $(\text{C}_6\text{F}_5)\text{Co}(\text{dotnH}) X (X = \text{Br}, \text{I}, \text{CN})$ show an initial loss of weight corresponding to the breaking of the cobalt-carbon bond, the C_6F_5 group being eliminated as decafluoro biphenyl $\text{C}_{12}\text{F}_{10}$. The cobalt(II) complex

Table 3

Temperature ranges observed in thermal decomposition of $(\text{C}_6\text{F}_5)\text{Co}(\text{dotnH}) X$

<i>X</i>	Medium	- C_6F_5		Nature of transformation
Br	N_2	136	167	exo
I	N_2	104	130	exo
I	air	104	130	exo
CN	N_2	118	139	exo

so formed rapidly decomposes, but the decomposition products were not investigated. It was observed that elimination of the organic radical does not take place homogeneously. Two differentiated stages are observed for half of the TG curves, this pattern being particularly clear in the iodo and cyano derivatives.

Kinetic study

Activation energy values for elimination of the organic radical from several complexes and for elimination of the amine in the particular case of the complex with mesalen and pyridine were calculated by the Freeman and Carroll method [7].

Table 4

Kinetic parameters for different types of thermal decomposition reactions

Complex	<i>n</i>	E_a (Kcal/mole)	Reaction
$(\text{C}_6\text{F}_5)\text{Co}(\text{acacen})$	0.1	43.47	b,
$(\text{C}_6\text{F}_5)\text{Co}(\text{mesalen})$	0.1-0.2	40.15	b,
$(\text{C}_6\text{F}_5)\text{Co}(\text{mesalen})\text{py}$	0.1	23.40	a,
$(\text{C}_6\text{F}_5)\text{Co}(\text{dotnH})\text{Br}$	0.9-1.0	69.0	$(\text{C}_6\text{F}_5)\text{Co}(\text{dotnH})\text{Br} \rightarrow \text{C}_{12}\text{F}_{10} + \text{Co}(\text{dotnH})\text{Br}$

These kinetic parameters cannot be calculated for similar hexacoordinate complexes with acacen, because processes *a*) and *b*) take place simultaneously in these compounds.

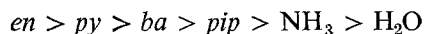
The results obtained are presented in Table 4.

Discussion

From a study of the TG and DTA data obtained for complexes of the type $(C_6F_5)CoL_4B$, where $L_4 =$ acacen, mesalen and dotnH, and B is a Lewis base, information can be inferred concerning the stabilities of the cobalt-carbon and cobalt-axial base bonds and the influence of the nature of the equatorial ligands on the process of thermal decomposition.

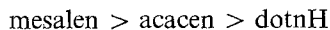
The hexacoordinate complexes derived from acacen and mesalen have octahedral configurations and, as observed in several studies [6], exhibit a marked tendency to pentacoordination. Considering the relatively low temperatures at which the hexacoordinate complexes derived from the acacen and mesalen ligands begin to lose the axial base, it may be said that in effect these complexes are easily converted into pentacoordinate ones which show an appreciable stability.

Moreover, by observing the temperatures at which decompositions begin, one can see that the stability of the cobalt-axial base bond for both types of complexes decreases in the following order:



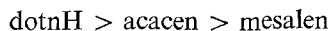
As regards the influence of the equatorial ligands, it was observed that the hexacoordinate complexes of acacen exhibit a greater tendency to pentacoordination than those with mesalen, in contrast with other reports [6]. However, the temperature difference is fairly small and no clear differentiation can be established.

In connection with the cobalt-carbon bond stability, it was observed that the greatest stability is displayed by the complexes of mesalen (240–250°), and that the stability order related to the nature of the ligand is



The values of the activation energies are not in general very informative, because these data are average values reflecting the overall effect of the thermal reaction; hence, in complex processes with overlapping thermal effects the scattering of the calculated values of E_a is high.

The E_a values for the carbon-cobalt bond-breaking reaction decrease in the order (Table 4)



An explanation for this pattern taking into account the stability of the cobalt-carbon bond can be found by considering the following:

- 1) The rupture of the cobalt-carbon bond occurs in a hexacoordinate species for

complexes with dotnH, whilst it occurs in a pentacoordinate species for complexes with acacen and mesalen because they have previously eliminated the axial base.

2) As the formation of the pentacoordinate species is unfavorable for complexes with dotnH, the coordination position vacant after the elimination of C_6F_5 must presumably be occupied by the anion in the trans position of a different molecule, forming a bridge between two cobalt atoms, both of which retain their maximum coordination number.

Thus, the second C_6F_5 radical is eliminated from a different substrate and at a different rate. This interpretation is confirmed by the observation of two different parts in the decomposition curves of complexes with I and CN, which have higher capacities to form bridge bonds than Br.

Finally, E_a values for process *b*) are higher than those for process *a*), following the order observed for the thermal stability.

References

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RÉSUMÉ — Afin d'obtenir des données sur le mécanisme de décomposition et l'influence des ligands sur la stabilité thermique des liaisons à base axiale cobalt et carbone-cobalt, on a étudié par TG et ATD une série de complexes du type $(C_6F_5)CoL_4B$, avec des ligands tétradentés ($L_4 =$ acasène, mésalène; $B = H_2O, NH_3, py, ba, pip, en$ et $L_4 = dotnH, B = Br, I, CN$).

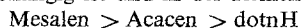
L'élimination de la base axiale conduit à la formation de complexes pentacoordinés $(C_6F_5)CoL_4$ (où $L_4 =$ acacène, mésalène) et leur décomposition subséquente fait intervenir la rupture de la liaison cobalt-carbone pour former CoL_4 . Cette dernière réaction intervient au contraire en premier lieu si le ligand tétradenté est dotnH.

On a observé que la stabilité de la liaison cobalt-carbone est en rapport avec la nature des ligands équatoriaux et diminue dans l'ordre suivant: mésalène > acacène > dotnH.

ZUSAMMENFASSUNG — Eine Reihe von Komplexen des Type $(C_6F_5)CoL_4B$ mit Tetridentat-Liganden ($L_4 =$ Acacen(N-N'Äthylen-bis-Acetylacetoniminat-Dianion), Mesalen (N-N'Äthylen-bis-7-7'-Dimethylsilylideniminat-Dianion); $B = H_2O, NH_3, py, ba, pip, en$ und $L_4 = dotnH$ (Diacetylmonoxym-imino-diacetylmonoxymat-iminopropan 1,3 Monoanion) $B = Br, I, CN$) wurde mittels TG und DTA Methoden untersucht, um Informationen bezüglich des Zersetzungsmechanismus und des Einflusses der Liganden auf die thermische Stabilität von Cobalt-Kohlenstoff- und Cobalt Axialbasenbindungen zu erhalten.

Die Eliminierung der axialen Base führt zur Bildung von Pentakoordinat-Komplexen $(C_6F_5)CoL_4$ (wobei $L_4 =$ Acacen, Mesalen) und ihre darauffolgende Zersetzung ist mit der Spaltung der Cobalt-Kohlenstoffbindung verbunden unter Bildung von CoL_4 . Im Gegensatz hierzu verläuft die letztere Reaktion zuerst, falls der Tetridentat-Ligand dotnH ist.

Es wurde beobachtet, daß die Stabilität von Kobalt-Kohlenstoffbindungen von der Art der äquatorialen Liganden abhängig ist und in der Reihenfolge



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Резюме — Ряд комплексов типа $(C_6F_5)_2CoL_4B$ с тетракоординируемыми лигандами ($L_4 = \text{аацен} — \text{дианион } N,N\text{-этиленбис-ацетилацетонимината, месален} — \text{дианион } N,N\text{-этиленбис-7,7-диметилсалицилиденимината}$); $B = H_2O, NH_3, py, ba, pip, en$ и $L_4 = \text{dotnH-анион диацетилмонооксим имино-диацетилмонооксимат-имино-пропана-1,3}$; $B = Br, I, CN$) был изучен, используя методы ТГ и ДТА, с целью получения информации относительно механизма разложения и влияния лигандов на термическую стабильность связей кобальт-углерод и кобальт-аксиальное основание. Удаление аксиального основания приводит к образованию пятикоординационных комплексов $(C_6F_5)_2CoL_4$, когда $L_4 = \text{аацен, месален}$, а их последующее разложение включает разрыв связи кобальт-углерод с образованием CoL_4 . Однако, эта реакция происходит сначала, когда лигандом является dotnH. Установлено, что стабильность связи кобальт-углерод связана с природой экваториальных лигандов и уменьшается в ряду месален > аацен > dotnH.