THERMAL DECOMPOSITION AND STABILITY IN A SERIES OF HETEROBIMETALLIC CARBONYL COMPOUNDS OF THE TYPE $[FE(CO)_4(HGX)_2]$ (X=CL, BR, I)

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ABSTRACT: Heterobimetallic carbonyl compounds of the type $[Fe(CO)_4(HgX)_2]$ (X= Cl, Br, I), which have metal-metal bonds, have been prepared in order to study their thermal stabilities as a function of the halogen coordinated to mercury atoms. The characterization of the above complexes was carried out by elemental analysis, **IR** and **NMR** spectroscopies. Their thermal behaviour has been investigated and the final product was identified by **IR** spectroscopy and by X-ray powder diffractogram.

KEYWORDS: thermal analysis; spectroscopy; metal carbonyls; iron; mercury; halogen.

Introduction

Reactions of transition - metal complexes with mercury salts have yielded a number of compounds which show metal-mercury bonds[4,10-13]. Among the first ones reported in the chemistry of metal- carbonyls are those compounds with Fe-Hg bonds like $[Fe(CO)_4(HgX)_2]$, X = Cl, Br, I [7,8]. Bimetallic compounds are now widely investigated for their improved properties[3,9,16] when compared with homometallic compounds. The reasons for carrying out the present work include our interest in the physical and chemical properties of bimetallic and mixed polinuclear transition metal compounds which render possible applications in catalysis and in devices for electron transport. Despite the intensive studies concerning to the synthesis and spectroscopic characterization of metal- carbonyls, it is noted that they have been scarcely investigated by thermogravimetric technique. In order to fill up this gap, and as a part of our on going studies of bimetallic compounds, we report herein our data related to thermal stability of the compounds $[Fe(CO)_4(HgX)_2]$; X = Cl **(1)**, Br**(2)**, I **(3)**.

Experimental

Thermal analysis was carried out using a Perkin-Elmer TGS-2 thermobalance. Samples of approximately 0.7mg were used, heated at a rate of 20 ° $C.min^{-1}$ in synthetic air.

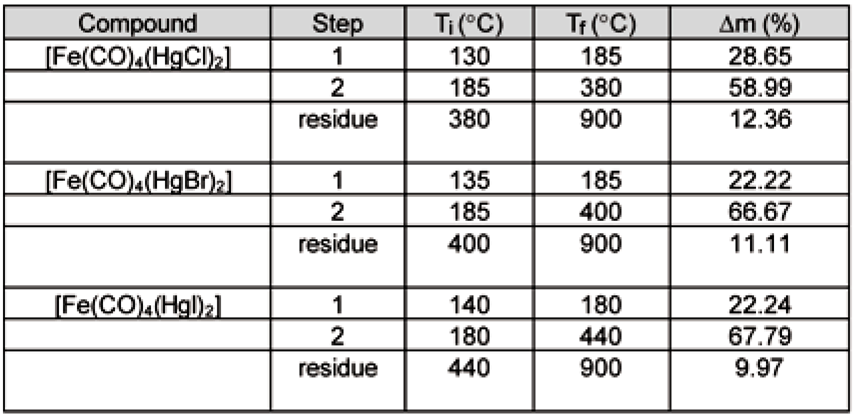
The **IR** spectra were recorded on a Nicolet 730 SX-FT spectrophotometer as an acetronitrile solution. The ^{199}Hg NMR spectra were obtained as DMSO/acetone solution (2:1,v:v) and referred to $HgCl_2$ (internal standard), on a Brucker AC-200 spectrometer operating at 81 MHz.

The complexes were prepared and analyzed as previously described[17].

Results and discussion

There has been recently an increase interest in the application of thermal analysis for studies of metal- carbonyl compounds[1,2]. In this work the use of thermogravimetric analysis has as its main objectives to verify the influence of the HgX moiety, X = Cl**(1)**, Br**(2)**, I**(3)** on the initial decomposition temperature and on the thermal decomposition mechanisms. Table 1 gives the steps, initial and final temperatures (° C), partial and total weight losses (%) for the thermal decompositions of **1**, **2** and **3**, in dry air atmosphere. The TG curves for these compounds under dry air atmosphere are illustrated in Fig.1

Table 1- Thermal analysis data for compounds **1-3**



Compound	Step	T_i (°C)	T_f (°C)	Δm (%)
$[Fe(CO)_4(HgCl)_2]$	1	130	185	28.65
	2	185	380	58.99
	residue	380	900	12.36
$[Fe(CO)_4(HgBr)_2]$	1	135	185	22.22
	2	185	400	66.67
	residue	400	900	11.11
$[Fe(CO)_4(HgI)_2]$	1	140	180	22.24
	2	180	440	67.79
	residue	440	900	9.97

T_i = initial temperature; T_f = final temperature, Δm = mass variation; total porcentual mass losses are showed in parentheses for each compound.

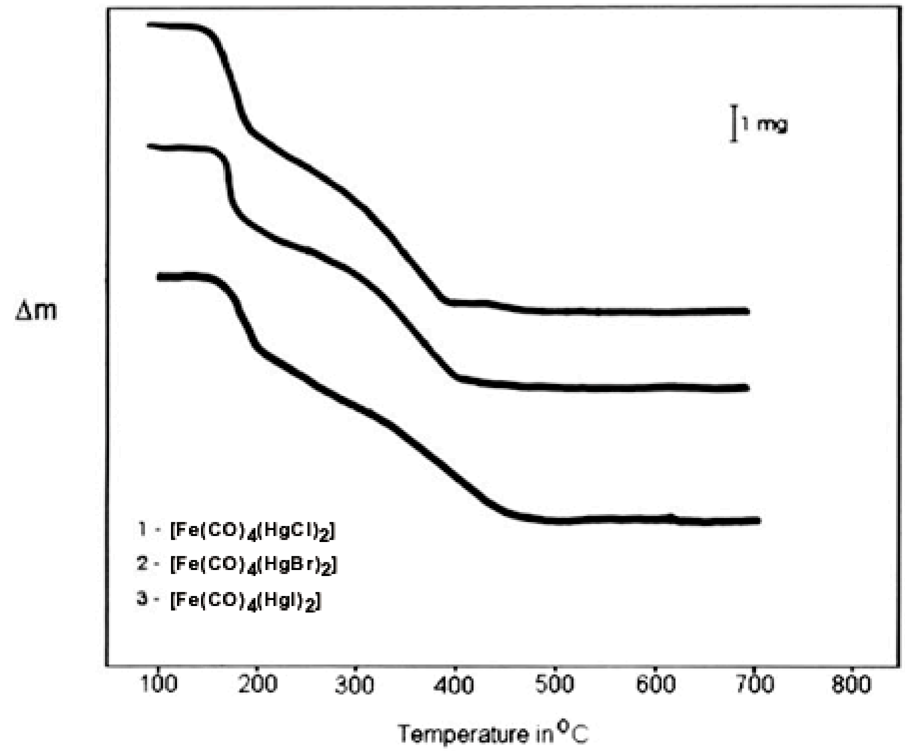


FIGURE 1 – TG curves of the compounds : 1-$[Fe(CO)_4(HgCl)_2]$; 2-$[Fe(CO)_4(HgBr)_2]$; 3-$[Fe(CO)_4(HgI)_2]$.

The thermal decomposition of **1** occurs in two consecutive steps. The first mass loss occurs between 130-185° C corresponding to, by mass calculation, the loss of four CO groups and of a Cl_2 molecule. In the temperature range of 185-380° C the mass loss observed is due to sublimation of the two Hg atoms and the uptake of O_2. The residue was identified as being Fe_2O_3 by **IR** spectroscopy[6,14] and X-ray powder diagram[15] (ASTM card file 24-0072).

The **TG** curve of **2** shows that its thermal degradation starts at 135° C. The first decomposition step suggests, by mass calculation, the loss of three CO groups and of a bromine atom ($1/2Br_2$). In the second step, in the range 185-400° C, there is the mass loss of a CO group; of a bromine atom ($1/2Br_2$), the complete sublimation of mercury atoms (2Hg) and the uptake of O_2. A constant mass was reached at 900° C, and the residue was identified as Fe_2O_3, as before.

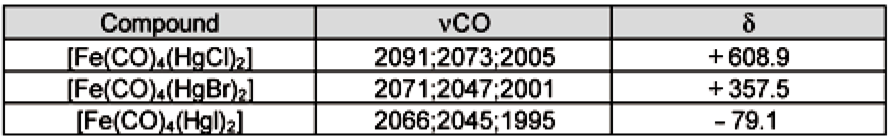
The thermal decomposition of **3** starts at 140° C and comprises two consecutives steps. The first mass loss, between 140 - 180° C, is assigned to, by mass calculation, the elimination of two CO groups and of an iodine atom ($1/2I_2$). The final step, in the range 180 - 440° C, suggests, by mass calculation, the loss of two CO groups, of an iodine atom ($1/2I_2$), the complete sublimation of mercury (2Hg) and the uptake of oxygen. The residue was showed to be Fe_2O_3, as before.

Summarizing the above results it was observed the loss of all CO groups for **1** at the beginning of the decomposition process, while the compounds **2** and **3** liberate these groups in two steps. Moreover, taking into account the initial temperature of the decomposition processes, it was possible to establish the following relative thermal stability order: **3**>**2**>**1**. As to the halide coordinated to the Hg atoms is noted that as its soft character increases the more stable the compound is.

It is instructive at this point to relate the precedent results with those of spectroscopic investigation. Concerning to the strength of the Fe-C bonds the **TG** data showed that the order is as follows: **3** >**2** >**1**, what is equivalent to say, taking into account the characteristics[5] of the iron-carbon monoxide bonding, that for the CO bonds the order is **1**>**2**>**3**.

The CO stretching vibrations are the most characteristic ones for the metal- carbonyls and their values for the compounds $[Fe(CO)_4(HgX)_2]$ are given in table 2. An important feature of note is that for the νCO frequencies the order is **1**>**2**>**3**, indicating in this way a total agreement with the **TG** data.

Table 2- Frequencies of νCO (cm^{-1}) and δ (ppm) ^{199}Hg for compounds **1-3**



Compound	νCO	δ
$[Fe(CO)_4(HgCl)_2]$	2091;2073;2005	+608.9
$[Fe(CO)_4(HgBr)_2]$	2071;2047;2001	+357.5
$[Fe(CO)_4(HgI)_2]$	2066;2045;1995	-79.1

A plausible explanation for this fact relies on the difference of back-donation from the iron to the CO groups along the series $[Fe(CO)_4(HgX)_2]$. Iodine being the softest base forms the strongest bond to Hg atoms, leading to, as a consequence, an increase in the electron density at the iron atom in the compound $[Fe(CO)_4(HgI)_2]$. Therefore this compound presents the greatest transfer of electron density to CO π* orbitals, likely the **IR** data have clearly indicated.

The ^{199}Hg NMR spectra give further evidence for the above conclusion. The chemical shift indicate that as the eletronegativity of the halide group decreases the more protect the Hg atoms are. In this way as the electron density on the Hg atoms increases, there is less transfer of electron density from iron to mercury atoms, leading finally to an increase in the strength of Fe-C bonds in the order **3** >**2** >**1**, as **TG** and **IR** data showed.

Conclusion

In this work the thermogravimetric study of the compounds $[Fe(CO)_4(HgX)_2]$, X = Cl, Br , I , has proved the influence of the HgX group on their thermal stabilities. In addition it was observed a strictly agreement of the thermogravimetric data with those given by **IR** and **NMR** spectroscopies.

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ZAMIAN, J.R. et al. decomposição Térmica e Estabilidade na Série de Compostos Carbonílicos Heterobimetálicos do Tipo $[Fe(CO)_4(HgX)_2]$ (X=Cl, Br, I). *Ecl. Quím. (São Paulo)*, v.25, p. , 2000

RESUMO: *Foram preparados compostos carbonílicos heterobimetálicos do tipo* $[Fe(CO)_4(HgX)_2]$ *(X= Cl, Br, I), contendo ligação metal-metal, objetivando investigar suas estabilidades térmicas em função do halogênio coordenado aos átomos de mercúrio. A caracterização destes complexos foi feita usando-se de técnicas espectroscópicas de infravermelho e ressonância magnética nuclear, além de análise elementar. O produto final das termodecomposições foi identificado através de espectroscopia no infravermelho e difratograma de raios-X, método de pó.*
PALAVRAS-CHAVE: *análise térmica; espectroscopia; carbonil-metais; ferro; mercúrio; halogênio.*

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