THERMAL DECOMPOSITION AND STABILITY OF [Fe(η^4-ENONE)(CO)$_2$L] COMPLEXES (*L*=CO AND PPh$_3$)

K. Zutin, V. M. Nogueira[*]*, A. E. Mauro, G. R. de Souza and S. I. Klein*

Instituto de Química de Araraquara, UNESP, São Paulo State University, Araraquara, São Paulo, C.P. 355, CEP 14800-900, Brazil

The compounds [Fe(bda)(CO)$_2$L] and [Fe(ch)(CO)$_2$L], (*bda*=benzylideneacetone; *ch*=chalcone; *L*=CO, PPh$_3$) were investigated by thermogravimetry and derivative thermogravimetry (TG and DTG). The fragmentation patterns suggest that the iron atom protects the enone fragment, so that the organic ligands break up with the loss of the pendant aromatic rings.

Introduction

Iron tricarbonyl derivates of α, β unsatured ketones, provide a convenient source of the 'Fe(CO)$_3$' moiety, and their synthesis offers some advantages over the conventional methods of preparation of complexes containing such fragment [1–6].

The reactions of [Fe$_2$(CO)$_9$] with benzylideneacetone (*bda*) and chalcone (*ch*) (Fig. 1) were studied by Howell *et al.* [7], which prepared the corresponding [Fe(η^4-enone)(CO)$_4$]; of these, they observed that [Fe(bda)(CO)$_4$] was less stable than the chalcone derivative, and readily loosed a carbonyl ligand to be converted to [Fe(bda)(CO)$_3$].

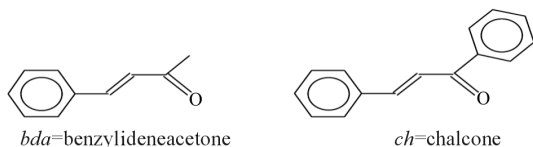*bda*=benzylideneacetone   *ch*=chalcone

Fig. 1 Structure of *bda* and *ch*

The substitution of one or more carbonyls in these compounds by triphenylphosphane is of particular interest, because the electronic and steric properties of this ligand would severely modify the metal environment, and such changes could eventually help in the understanding of the nature of the iron-diene bonds [8]. However, the reactions of the tricarbonyl complex with phosphanes generally lead to the uncoordination of the keto end of the enone, rendering a monoolefine complex, or to the complete removal of the heterodiene [9]. Only upon irradiation of benzene solutions of [Fe(CO)$_4$PPh$_3$] or [Fe(CO)$_3$(PPh$_3$)$_2$] in the presence of benzylideneacetone, [Fe(bda)(CO)$_2$PPh$_3$] can be prepared in good yields [10]. Although the preparation and studies of these complexes have been reported several times [8, 10–16], to our knowledge, no thermal behavior of such species have been reported, neither any attempt to relate that thermal behavior with the very important parameters such as structure and metal-olefin bonding. In the present paper we report the preparation, IR and ^{31}P NMR spectroscopic characterization and thermal stability of the tricarbonyltriphenylphosphaneiron and dicarbonyltriphenylphosphane-iron complexes containing bda or ch ligands.

Experimental

Preparation of complexes

All reactions were carried out in dry solvents under nitrogen atmosphere.

[Fe(enone)(CO)$_3$] (enone is *bda* or *ch*) were prepared by slight modification of the previously described procedure [7]. Enone (2.7 mmol) and Fe$_2$CO$_9$ (2.7 mmol) were heated in benzene (15 mL) for 4 h at 40–50°C. The resulting solutions were filtered and the solvent was removed under vacuum. The residues were chromatographed on silica gel. Elution with 10% ethyl acetate–benzene gave, after cooling and recrystallization from *n*-pentane, the products [Fe(ch)(CO)$_3$] and [Fe(bda)(CO)$_3$] as yellow to yellow reddish crystals. Orange crystals (25% yield based on *ch*) of the complex [Fe(ch)(CO)$_2$PPh$_3$] were obtained according to published methods [15, 17].

Instrumentation

Infrared spectra (IR) were recorded on a Nicolet Impact 400 spectrophotometer in the spectral range

---

[*]   Author for correspondence: vaniamn@iq.unesp.br

4000–400 cm^{-1} with the samples pressed in KBr discs. ^{31}P NMR spectra were obtained at 81.03 MHz as CDCl$_3$ solutions and referred to external 85% H$_3$PO$_4$ on a Bruker AC-200 spectrometer.

TG curves were carried out using a Mettler TA 4000 thermal analysis system, with a heating rate of 20°C min^{-1} in synthetic air. The intermediate residues of thermal decomposition were obtained on an Edgcon-5P hearth.

The X-ray diffractograms were obtained with a Verb Freiberg Prazionsmechanik, model HGZ4/B, using CuK$_\alpha$ radiation. The peaks were identified using ASTM data files.

Results and discussion

Infrared and ^{31}P NMR spectroscopic data are summarized in Table 1. The results for the complexes [Fe(bda)(CO)$_3$], [Fe(ch)(CO)$_3$] and [Fe(bda)(CO)$_2$PPh$_3$] were in good agreement with previous studies. The infrared spectra of the [Fe(ch)(CO)$_2$PPh$_3$] showed two strong ν_{CO} bands in the region 1920–2005 cm^{-1} typical of [Fe(enones)(CO)$_2$PPh$_3$] complexes [7, 8, 10]. Its ^{31}P NMR in CDCl$_3$ exhibited a peak at δ=52.20 that confirmed the phosphorus coordination.

The thermogravimetry (TG and DTG) data for the synthesized compounds are reported in Table 2.

TG and DTG curves for all the complexes (Fig. 2) in the temperature range of 50–550°C showed that [Fe(enone)(CO)$_3$] were thermally stable only below 50°C, whereas for the [Fe(enone)(CO)$_2$PPh$_3$] complexes, the thermal decomposition begun above 100°C.

It was interesting to note that for all compounds the thermal decomposition occurred in three steps, albeit with clearly different mechanisms, depending crucially on the enone employed. For the [Fe(ch)(CO)$_3$] complex it occurred the loss of one CO group during the first decomposition step, while for [Fe(bda)(CO)$_3$], a fragment of the organic ligand was lost first, with a CO molecule leaving only at the second decomposition step.

Accordingly, the IR spectrum (Table 3) of the [Fe(ch)(CO)$_3$] residue obtained at 134°C showed the disappearance of the ν_{CO} at 2000 cm^{-1} and some minor modifications in stretchings of the coordinated chalcone near 1500 cm^{-1} ($\nu_{C=O}$) and at 3050 cm^{-1} (ν_{CH} aromatic). The IR spectrum of the residue of this compound obtained after the second decomposition step at 408°C, showed the disappearance of the chalcone's aromatic bands near 3050 cm^{-1}. The remaining, small band at 1990 cm^{-1} in that spectrum still suggested the presence of a coordinated CO.

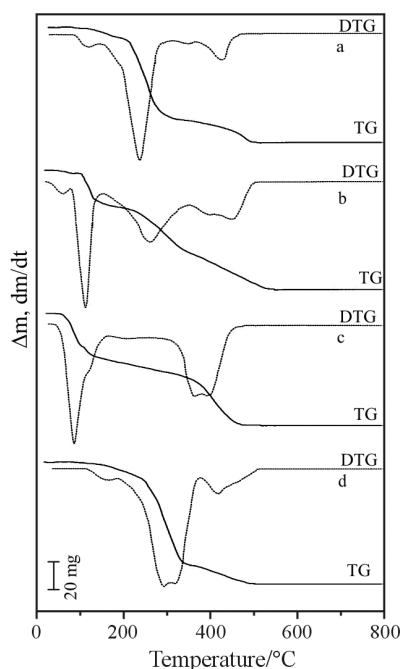**Table 1** IR (cm^{-1}) and NMR spectral data for complexes studied

Compounds	ν_{CO}	ν_{C-H} arom	$\nu_{C=C}$ arom	$\delta_{C=C,C-H}$ arom	ν_{C-H} alif	$\nu_{C=C,C=O}$ α, β conj	δ_{C-H} alif	δ ^{31}P
bda						1690, 1615		
ch						1670, 1610		
PPh$_3$								−3.05
[Fe(bda)(CO)$_3$]	2060, 1970	3050	1600–1400	1100–800	2900	1500–1380	1370	
[Fe(ch)(CO)$_3$]	2070, 2000	3045	1600–1400	1100–800	2900	1500–1380		
[Fe(bda)(CO)$_2$PPh$_3$]	2000, 1930							51.70
[Fe(ch)(CO)$_2$PPh$_3$]	2005, 1920							52.20

Table 2 Thermoanalytical data

Compounds	ΔT/°C	Mass loss/%		Product
		exp.	calcd.	
[Fe(bda)(CO)$_3$] m_{inic}=6.710 mg	50–129	27.57	27.27	C$_6$H$_6$
	129–229	9.81	9.79	CO
	229–550	43.89	43.79	C$_4$OH$_5$+2CO, with formation of Fe^0
[Fe(ch)(CO)$_3$] m_{inic}=7.684 mg	50–134	20.22	20.20	H$_2$O+2CO
	134–408	45.40	45.30	C$_{12}$H$_{10}$+0.5CO
	408–520	18.65	18.67	C$_3$OH$_2$+0.5CO, with formation of Fe^0
[Fe(bda)(CO)$_2$PPh$_3$] m_{inic}=6.860 mg	100–172	5.38	5.38	CO
	172–344	63.15	63.13	C$_{21}$PH$_{21}$+CO
	344–550	15.61	16.13	C$_7$OH$_8$, with formation of Fe$_2$O$_3$
[Fe(ch)(CO)$_2$PPh$_3$] m_{inic}=7.013 mg	125–212	4.86	4.81	CO
	212–384	69.23	69.37	C$_{30}$H$_{30}$+CO
	384–550	11.17	10.13	C$_3$H$_2$OP, with formation of Fe$_2$O$_3$

Table 3 IR (cm^{-1}) spectral data for thermal decomposition residues

Compound	$\Delta T/°C$	ν_{CO}	$\nu_{C-H\ arom}$	$\nu_{C=C,C=O\ \alpha,\ \beta\ conj}$
$[Fe(bda)(CO)_3]$	50–129	1970, 2060	–	1600, 1480
	129–229	1970, –	–	–, 1480
	229–550	–	–	–, 1480(w)
$[Fe(ch)(CO)_3]$	50–134	–, 2070	–	1850, 1750
	134–408	1900 (w)	–	–
	408–550	–	–	–
$[Fe(bda)(CO)_2PPh_3]$	100–172	2000, –		
	172–344	–		
	344–550	–		
$[Fe(ch)(CO)_2PPh_3]$	125–212	2000, –		
	212–384	–		
	384–550	–		

Fig. 2 TG and DTG curves of a – $[Fe(bda)(CO)_3]$, b – $[Fe(ch)(CO)_3]$, c – $[Fe(bda)(CO)_2PPh_3]$ and d – $[Fe(ch)(CO)_2PPh_3]$

The IR spectrum of the residue of $[Fe(bda)(CO)_3]$ obtained at 129°C exhibited changes right in the regions where the uncoordinated portion of the *bda* ligand typically absorbs that radiation; while the ν_{CO} bands of the coordinated *bda* and CO ligands remained (1500–1380, 1970 and 2060 cm^{-1}), the band near 3050 cm^{-1}, typical of the attached aromatic ring, disappeared. These results seem to be in very good agreement with the TG mass loss proposition that a C_6H_6 fragment is the leaving group in the first step of heating of the *bda* complex. Only after heating the sample up to 229°C that the disappearance of the CO band at 2060 cm^{-1} was observed in the IR spectrum of the residue. We accordingly assigned this as the second thermal decomposition step for $[Fe(ch)CO_3]$.

Heating both tricarbonyl(enone) complexes up to 550°C caused the complete loss of both CO groups and remaining organic fragments, with the probable formation of metallic iron. Above that temperature, the observed formation of Fe_2O_3 was confirmed by X-ray diffractometry (Fig. 3).

TG and DTG curves of both complexes $[Fe(bda)(CO)_2PPh_3]$ and $[Fe(ch)(CO)_2PPh_3]$ suggested that the thermal decomposition always begun with a loss of one CO group at the very first step of heating. In a manner that is different from the tricarbonyl series, this step is followed by the concomitant loss of the remaining CO group and the partial, mixed decomposition of the organic and the phosphorous ligands, under circumstances which are, again, dependent upon the enone employed. For instance, it is proposed that a phosphorus containing fragment is lost during the second step of the thermal decomposition of the compound with *bda*, but only at the last step for the *ch* complex. In the final stages of degradation, at temperatures up to 550°C, occurred again the loss of whatever remaining organic fragments and the subsequent formation of Fe_2O_3.
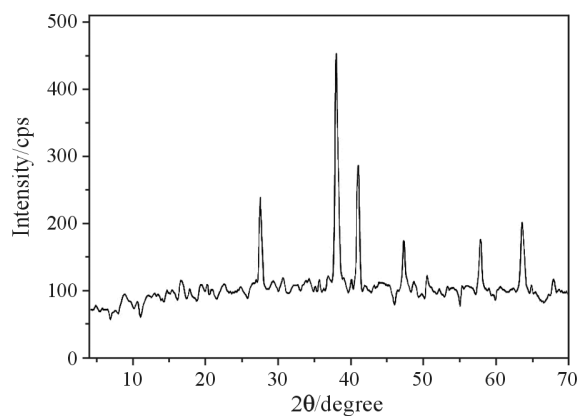
Fig. 3 X-ray of the final decomposition residue

Conclusions

The thermal behaviour of the four complexes discussed in this work is perhaps difficult to understand separately, but they show collectively that the iron-enone entity is the primal feature for all these compounds. This basic characteristic is clearly reflected by the last fragments that leave the metal under the extreme conditions of temperature imposed upon the compounds in the herewith called third step of thermal decomposition.

Theoretically, (Table 2), the final residue remaining on the metal in the tricarbonyl(enone) compounds have the basic composition 'C$_3$O' (enone=*ch*) and 'C$_4$O' (enone=*bda*), which probably reflect α,β-'unsaturated substrates' of the type 'O=C–C=C', from the loss of both aromatic rings of *ch*, and 'C–C(=O)–C=C', from the loss of the unique aromatic ring available in *bda*. Of course, there is no possibility as yet to determine the kinds of bonds that still hold those metal–organic fragments together, but they shall be very different from the η^4-mode as observed in the parent complexes [17–19].

The successive losses of pendant aromatic rings and CO molecules from this class of complexes upon heating is therefore a clear evidence of the strength of the Fe(O=C–C=C) interactions; it should be stressed, however, that the apparent stability of the σ-framework H$_3$C–C(=O)–C(H)=C(H)– of *dba* (Table 2) may be responsible for the TG suggested mechanism where the loss of a phenylic residue seem to be more important at the beginning of the decomposition pathway of [Fe(bda)(CO)$_3$] than the loss of a coordinated CO molecule.

The presence of one molecule of coordinated triphenylphosphane in [Fe(enone)(CO)$_2$PPh$_3$] does make very difficult any assumption regarding the thermal fragmentation pathway for those compounds, after the initial loss of one CO, regardless of the enone employed. Nevertheless, it is symptomatic that in the *ch* case, where there is the possibility of thermal detachment of two aromatic rings, as before, the final residue seem to contain a residual phosphorous atom embedded in the ubiquitous 'O=C–C=C' fragment (Table 2), whereas for the *bda* analog, the final organic fragments include that which can also be regarded as arising from the metal-stabilized C–C(=O)–C=C. The combined results for the thermal decomposition of this whole family of compounds seem therefore to be reflecting both the metal to enone strong α and π interactions, in accordance to the well established Chatt, Duncanson and Levason synergistic model of bonding [20], and the internal stability of the α-framework of the α,β-unsaturated ligand.

References

1 D. H. R. Barton, A. A. L. Gunatilaka, T. Nakanishi, H. Patin, W. A. Barton and B. R. Worth, J. C. S. Perkin I, 8 (1976) 821.
2 G. Sholes, C. R. Graham and M. Brookhart, J. Am. Chem. Soc., 96 (1974) 5665.
3 M. Brookhart, G. O. Nelson, G. Scholes and R. A. Watson, J. C. S. Chem. Comm., 6 (1976) 195.
4 B. F. G. Johson, J. Lewis, P. McArdle and G. L. P. Randall, Chem. Comm., 2 (1971) 177.
5 G. D. Sargent, N. Lowry and S. D. Reich, J. Amer. Chem. Soc., 89 (1967) 5985.
6 C. R. Ganellin and R. Petit, J. Chem. Soc., 112 (1958) 576.
7 J. A. S. Howell, B. F. G. Johnson, P. L. Josty and J. Lewis, J. Organomet. Chem., 39 (1972) 329.
8 E. J. S. Vichi, P. R. Raithby and M. McPartlin, J. Organomet. Chem., 256 (1983) 111.
9 A. Vessieres and P. Dixneuf, Tetrahedron Lett., 16 (1974) 1499.
10 B. F. G. Johnson, J. Lewis, G. R. Stephenson and E. J. S. Vichi, J. Chem. Soc., Dalton Trans., 5 (1978) 369.
11 E. J. S. Vichi, F. Y. Fujiwara and E. Stein, Inorg. Chem., 24 (1985) 286.
12 J. A. S. Howell, D. T. Dixon and J. C. Kole, J. Organomet. Chem., 69 (1984) 266.
13 M. J. Calhorda and E. J. S. Vichi, Organometallics, 9 (1990) 1060.
14 V. M. Nogueira, A. V. Benedetti, E. J. S. Vichi and E. Stein, J. Electroanal. Chem., 287 (1991) 761.
15 K. Zutin, V. M. Nogueira, A. E. Mauro, P. Melnikov and A. Iluykhin, Polyhedron, 20 (2001) 1011.
16 P. S. Haddad, A. E. Mauro, V. M. Nogueira and S. I. Klein, Trans. Metal Chem., 28 (2003) 899.
17 A. F. Clifford and A. K. Mukherjee, Inorg. Synth., 8 (1966) 185.
18 F. M. Chaudari and P. L. Pauson, J. Organomet. Chem., 5 (1966) 73.
19 R. Edwards, J. A. S. Howell, B. F. G. Johnson and J. Lewis, J. Chem. Soc. Dalton Trans., 19 (1974) 2105.
20 J. Chatt and L. A. Duncanson, J. Chem. Soc., (1953) 2939.