

(Sorbic acid)Fe(CO)₂L complexes with L = CO, P(OPh)₃, PPh₃, and PEt₃. Photolytic preparation, spectral properties, and bonding

Élvio H. Santos, Edison Stein, Eduardo J.S. Vichi *

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13081-Campinas-SP (Brasil)

and Elisa B. Saitovitch

Centro Brasileiro de Pesquisas Físicas, Conselho Nacional de Desenvolvimento Científico e Tecnológico, Rua Wenceslau Braz, 71, Rio de Janeiro (Brasil)

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Abstract

The (sorbic acid)Fe(CO)₂L complexes, with L = CO, P(OPh)₃, PPh₃ and PEt₃, have been prepared by irradiating the corresponding Fe(CO)₄L compounds in benzene in the presence of sorbic acid. The Mössbauer spectra are compatible with the structure of a tetragonal pyramid with the iron(0) atom located in the center of the base. The values of the isomer shift, δ , seem to indicate that $d_{\pi}-L_{\pi}^*$ back bonding is predominant for L = CO, significant for L = P(OPh)₃, and negligible for L = PPh₃ and PEt₃. The order of decrease of the frequencies $\nu(\text{C}=\text{O})$ of the coordinated sorbic acid parallels the order of increase of the σ -donor ability of L.

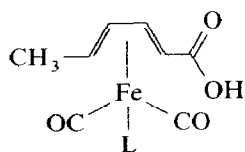
Introduction

The preparation of the (sorbic acid)tricarbonyliron(0) complex, (SBA)Fe(CO)₃, was first reported by Stone et al. [1]. A mixture of Fe₃(CO)₁₂ and sorbic acid was refluxed in benzene for several hours, and the product formed was identified in the reaction mixture by infrared. However, these workers failed to isolate the compound. Later, Cais and Maoz [2] succeeded in isolating the complex in poor yields, after refluxing Fe₃(CO)₁₂ and sorbic acid for 8 h in di-n-butyl ether.

The main limitation of these thermal methods is that free sorbic acid undergoes extensive polymerization at temperatures higher than ca. 50 °C.

In previous papers [3–5], we reported the photolytic preparation of (benzylideneacetone)dicarbonylphosphineiron(0) complexes which gave good yields of products. Here we describe the extension of this method to the preparation of

(SBA)Fe(CO)₂L complexes (1–4) and discuss the results of spectral studies on these complexes (1, L = CO; 2, L = P(OPh)₃; 3, L = PPh₃; 4, L = PEt₃).



(1–4)

The main advantage of this method is that sorbic acid reacts at room temperature in a short reaction time thereby preventing polymerization.

Experimental

The photolyses were carried out under dry dinitrogen in a glass annular reactor using a 125W medium-pressure mercury lamp. Infrared spectra were recorded on a Perkin–Elmer 257 spectrometer. Mass spectra were recorded on a Finnigan Instruments 1015 S/L spectrometer equipped with a 6100 MS data system.

The Mössbauer spectra were recorded in 1024 channels of a Hewlett–Packard multichannel analyser with a drive unit which provides a sinusoidal motion to the ⁵⁷Co source. The samples and the ⁵⁷Co source were kept in a cryostat at 100 K to improve the absorption in the Mössbauer spectra. The data folding and linearization were carried out on a 370/175 IBM computer; they were fitted assuming quadrupole doublets with symmetric pair of lines.

The potentiometric titrations were performed in a Metrohm E 500 potentiometer. The complexes were titrated with sodium hydroxide using a Methron EA 246 Ag/AgCl conjugated electrode.

Carbon and hydrogen microanalyses were carried out at the Research Center of Rhodia in Campinas, and iron was analysed in our laboratory.

Preparations

(Sorbic acid)tricarbonyliron(0). A solution of sorbic acid (2240 mg, 20 mmol) and Fe(CO)₅ (5.00 ml, 17 mmol) in benzene (250 ml) was irradiated for 2 h. The resulting mixture was filtered and the solvent was removed under vacuum. The resulting yellow-brown residue was recrystallized from methanol to give 1000 mg (25% based on Fe(CO)₅) of the product as a yellow powder (m.p. 141–142°C; Found: C, 42.79; H, 3.14; Fe, 22.38. C₉H₈FeO₅ calcd.: C, 42.89; H, 3.19; Fe, 22.16%. Mol. mass 252 (found in mass spectrum); calcd. 252.01).

(Sorbic acid)dicarbonyltriphenylphosphiteiron(0). A solution of sorbic acid (1000 mg; 8.9 mmol) and Fe(CO)₄P(OPh)₃ (1500 mg; 3.1 mmol) in benzene (250 ml) was irradiated for 3 h. The resulting mixture was filtered and the solvent was removed under vacuum. The resulting brown oil was recrystallized from methanol to give 580 mg (36% based on Fe(CO)₄P(OPh)₃) of the product as a yellow powder (m.p. 173–174°C; Found: C, 58.27; H, 4.19; Fe, 10.75. C₂₆H₂₃FeO₇P calcd.: C, 58.44; H, 4.33; Fe, 10.45%. Mol. mass, 534 (found in the mass spectrum); calcd. 534.28).

(Sorbic acid)dicarbonyltriphenylphosphineiron(0). A solution of sorbic acid (400 mg; 3.6 mmol) and Fe(CO)₄PPh₃ (430 mg; 1.0 mmol) in benzene (250 ml) was irradiated for 3 h. The resulting mixture was filtered and the solvent was removed under vacuum. The resulting yellow-green residue was recrystallized from methanol

to give 220 mg (45% based on $\text{Fe}(\text{CO})_4\text{PPh}_3$) of the product as a yellow powder (m.p.: 152–153°C; Found: C, 64.09; H, 4.71; Fe, 12.02. $\text{C}_{26}\text{H}_{23}\text{FeO}_4\text{P}$ calcd.: C, 64.22; H, 4.76; Fe, 11.48%. Mol.mass: 486 (found in mass spectrum); Calcd. 486.28).

(*Sorbic acid*)dicarbonyltriethylphosphineiron(0). A solution of sorbic acid (600 mg; 5.4 mmol) and $\text{Fe}(\text{CO})_4\text{PEt}_3$ (550 mg; 1.9 mmol) in benzene (250 ml) was irradiated for 3 h. The resulting mixture was filtered and the solvent was removed under vacuum. The resulting oil was recrystallized from methanol to give 370 mg (39% based on $\text{Fe}(\text{CO})_4\text{PEt}_3$) of a yellow powder (m.p. 183–184°C; Found: C, 48.98; H, 6.61; Fe, 17.01. $\text{C}_{14}\text{H}_{23}\text{FeO}_4\text{P}$ calcd.: C, 49.14; H, 6.87; Fe, 16.37%.

Results

The Mössbauer and infrared spectral data of the $(\text{SBA})\text{Fe}(\text{CO})_2\text{L}$ complexes and the values of $\text{p}K_a$ of the coordinated sorbic acid in these complexes are listed in Table 1.

The isomer shift values, δ (–0.056 to +0.006 mm/s), are in the range expected for iron(0) compounds and the quadrupole splitting values, ΔE_q (1.43 to 1.63 mm/s), are compatible with the tetragonal pyramid point symmetry revealed by an X-ray study of $(\text{SBA})\text{Fe}(\text{CO})_3$ [9].

The infrared spectra of the dicarbonyl derivatives show two strong and sharp $\nu(\text{C}\equiv\text{O})$ bands, of same intensity, in the region 2000–1945 cm^{-1} typical of $(\text{diene})\text{Fe}(\text{CO})_2\text{L}$ complexes [3,8,10] and one $\nu(\text{C}=\text{O})$ band in the region 1640–1660 cm^{-1} , assigned to the carbonyl group of the coordinated sorbic acid (1690 cm^{-1} in the free ligand).

The mass spectra show molecular peaks for the complexes with $\text{L} = \text{CO}$, $\text{P}(\text{OPh})_3$ and PPh_3 (see experimental). The higher m/e peak for the complex with $\text{L} = \text{PEt}_3$, found at m/e 286 is assigned to the $[(\text{SBA})\text{FePEt}_3]^+$ fragment. A peak at m/e 168, assigned to the $[(\text{SBA})\text{Fe}]^+$ fragment, is observed in the spectra of all complexes. This peak is very intense for the $(\text{SBA})\text{Fe}(\text{CO})_3$ complex but weak for the complexes with phosphorus ligands. Peaks at m/e 196, assigned to the $[(\text{SBA})\text{Fe}(\text{CO})]^+$ fragment, were observed in the spectra of the complexes with $\text{L} = \text{CO}$ and $\text{P}(\text{OPh})_3$ but not for $\text{L} = \text{PPh}_3$ or PEt_3 . A peak at m/e 224, assignable to the $[(\text{SBA})\text{Fe}(\text{CO})_2]^+$ fragment was observed only in the spectrum of the tricarbonyliron(0) complex. A peak at m/e 458, found in the spectrum of the complex with $\text{L} = \text{PPh}_3$, is assigned to the $[(\text{SBA})\text{Fe}(\text{CO})\text{PPh}_3]^+$ fragment.

Table 1

Mössbauer and infrared spectral data for the $(\text{SBA})\text{Fe}(\text{CO})_2\text{L}$ complexes and $\text{p}K_a$ values of coordinated sorbic acid in these complexes

Complex	δ (mm/s)	ΔE_q (mm/s)	$\nu(\text{C}=\text{O})$ (cm^{-1})	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})	$\text{p}K_a$	Ref.
$(\text{SBA})\text{Fe}(\text{CO})_3$	–0.049	1.63	1670	2100; 2050	7.20	this work
$(\text{SBA})\text{Fe}(\text{CO})_2\text{P}(\text{OPh})_3$	–0.034	1.57	1660	2000; 1950	7.50	this work
$(\text{SBA})\text{Fe}(\text{CO})_2\text{PPh}_3$	+0.006	1.43	1655	2005; 1945	7.55	this work
$(\text{SBA})\text{Fe}(\text{CO})_2\text{PEt}_3$	–0.056	1.51	1640	2000; 1950	7.65	this work
$(\text{Butadiene})\text{Fe}(\text{CO})_3$	–0.084	1.46	–	1973; 1910	–	6,7
Sorbic acid	–	–	1690	–	7.00	8

Discussion

According to the bonding scheme proposed for (diene)carbonylphosphineiron(0) complexes [5,11], the overall electron density at the metal atom is controlled by the interactions of the metal dsp hybrid orbitals with the HOMO and LUMO of the diene and with the σ and π orbitals of carbon monoxide and phosphorus ligands. The strongest interaction between the $\text{Fe}(\text{CO})_2\text{L}$ fragment and the diene is the π -back donation from a filled dsp orbital to the LUMO of the diene [12–15], the net result being an electron transfer from the iron carbonyl fragment to the diene. The relative contributions of σ and π bonding to the metal–phosphorus bond is discussed in several papers [16–18]. It appears that the phosphorus ligands cannot be characterized by definite donor–acceptor capacities, as these capacities are also dependent on the overall electron density of the complex to which they are bonded [17b].

It is established that in iron complexes both ligand to iron σ -bonding and iron to ligand π -back bonding increase the s electron density at the iron nucleus with a consequent decrease in the isomer shift, δ , obtained from the Mössbauer spectrum [19]. Through σ -bonding, electron density is transferred from the ligand to the proper iron orbitals which have, at least, partial $4s$ character. Through π -back bonding, d electrons of the metal are transferred to the ligands decreasing the shielding of the $3s$ electrons. So, δ measures the effect of $\sigma + \pi$ bonding on the s electron density at the iron nucleus.

An analysis of isomer shifts (δ) obtained in the closely related series of complexes studied in this work may help in evaluating the contribution of σ and π effects in these complexes.

First, it is interesting to compare the values of δ obtained for (butadiene) $\text{Fe}(\text{CO})_3$ (-0.084 mm/s) and (SBA) $\text{Fe}(\text{CO})_3$ (-0.049 mm/s). The isomer shift, is significantly less negative for (SBA) $\text{Fe}(\text{CO})_3$ indicating less s electron density in the iron nucleus in this complex. Since the strongest interaction between the $\text{Fe}(\text{CO})_2\text{L}$ fragment and the diene seems to be d_π – π_π^* back donation [12–14], these results may indicate that sorbic acid is a poorer π -acceptor than butadiene. This is consistent with the higher values of $\nu(\text{C}\equiv\text{O})$ of (SBA) $\text{Fe}(\text{CO})_3$ (2100 ; 2050 cm^{-1}) compared to (butadiene) $\text{Fe}(\text{CO})_3$ (1973 ; 1910 cm^{-1}).

From the values of δ obtained for the (SBA) $\text{Fe}(\text{CO})_2\text{L}$ complexes, the s electron density at the iron nucleus increases in the order of $\text{L} = \text{PPh}_3$ ($+0.006$ mm/s) $<$ $\text{P}(\text{OPh})_3$ (-0.034 mm/s) $<$ CO (-0.049 mm/s) $<$ PEt_3 (-0.056 mm/s). This order of increase of s electron density at the iron nucleus is not the order of increase in the basicity (σ -donor capacity) of free L, which is $\text{CO} < \text{P}(\text{OPh})_3 < \text{PPh}_3 < \text{PEt}_3$. The more negative value of δ for the (SBA) $\text{Fe}(\text{CO})_3$ complex compared to the PPh_3 and $\text{P}(\text{OPh})_3$ derivatives is probably due to the higher π -acidity of the CO ligand which, consequently, withdraw more electron density from the iron d orbitals than do the phosphorus ligands. The $d_\pi \rightarrow \pi_\pi^*$ back donation reduces the negative charge at the iron atom enhancing the σ -donor ability of bonded CO, both σ - and π -effects contributing synergically to the increased s electron density at the iron nucleus in the (SBA) $\text{Fe}(\text{CO})_3$ complex. The more negative value of δ in the PEt_3 complex compared to the PPh_3 derivative may be attributed mainly to σ -donation since PEt_3 ($\text{p}K_a = 8.69$) is much more basic than PPh_3 ($\text{p}K_a = 2.73$), and PEt_3 is less π -acidic than PPh_3 [20]. However, the $\text{P}(\text{OPh})_3$ ($\text{p}K_a = 1.17$) complex shows a more negative

value of δ than the PPh_3 derivative in spite of PPh_3 having a higher intrinsic basicity than P(OPh)_3 . This suggests a bigger $d_\pi-d_\pi$ interaction in the P(OPh)_3 derivative.

In summary, the Mössbauer results in this closely related series of $(\text{SBA})\text{Fe}(\text{CO})_2\text{L}$ complexes seem to indicate that $d_\pi-L_\pi$ interaction is predominant for $\text{L} = \text{CO}$, significant for $\text{L} = \text{P(OPh)}_3$ and negligible for $\text{L} = \text{PEt}_3$ and PPh_3 .

The decrease observed in the $\nu(\text{C}=\text{O})$ frequencies in the infrared spectra of SBA after coordination is expected since the $\text{Fe}(\text{CO})_2\text{L}$ moieties act as net electron donors to diene ligands [12–14]. The electronic effect of the $\text{Fe}(\text{CO})_2\text{L}$ groups is transmitted through the π -system of the coordinated SBA to the carboxylic carbonyl. The order of decrease of the frequencies $\nu(\text{C}=\text{O})$ parallels the order of increase of the basicity of the ligand L, viz. CO (1670 cm^{-1}) < P(OPh)_3 (1660 cm^{-1}) < PPh_3 (1655 cm^{-1}) < PEt_3 (1640 cm^{-1}).

The transmission of the electronic effect of L to the coordinated sorbic acid is also shown by the values of $\text{p}K_a$. Although the differences are small, the trend suggests that the acidity of the coordinated SBA decreases as the σ -donor ability of L increases.

The frequencies $\nu(\text{C}\equiv\text{O})$ are lower for the complexes with phosphorus ligands when compared to the tricarbonyl derivative. This would be expected when a CO ligand is substituted by a much better σ -donor and poorer π -acceptor phosphorus ligand. However there are no significant differences among the phosphorus complexes in spite of the ligands having different σ -donor abilities. This result and the trend in the $\nu(\text{C}=\text{O})$ frequencies discussed above suggest that most of the electronic effect of the phosphorus ligands is transmitted to the diene via a $\text{P} \xrightarrow{\sigma} \text{Fe} \xrightarrow{\pi} \text{SBA}$ mechanism.

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