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(η^2-CINNAMIC)TETRACARBONYLIRON ACIDS. SYNTHESIS AND ACIDITY

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Summary

(η^2-cinnamic)tetracarbonyliron acids [(η^2-$XC_6H_4CH{=}CHCOOH$) $Fe(CO)_4$] (X = H, 3-OMe, 4-OMe, 4-Me, 3-Cl, 4-Cl) have been prepared and their pK_a's measured spectrophotometrically. The measured acidities indicate that the [$Fe(CO)_4$] group is electron releasing. The effect of the substituent is explained by the break of conjugations in the olefinic substituent.

Introduction

The effect of complexation on the electronic characteristics and the reactivity of the organic group in organometallic complexes is of much interest [1]. The effects are connected with some problems of homogeneous catalysis in the presence of metals in the organic field, since metals can participate by changing the electron distribution in the organic molecule through formation of unstable adducts [2]. A simple way of studying these effects is to measure the acid dissociation constants of carboxyl groups bonded to the organic molecule, and several such studies have been reported [3]. The magnitudes and direction of these effects depend upon which metal is present, but it is not clear which properties of the metal are involved [4].

With the aim of investigating such effects, we have synthesized the complexes [$Fe(CO)_4$(η^2-$XC_6H_4CH{=}CHCOOH$)] (X = 4-Me, 4-Cl, 3-Cl, 4-OMe, 3-OMe, and H) and measured their acidities.

Results and discussion

Table 1 lists some physical properties of *meta*- and *para*-substituted cinnamic acids and their complexes with [$Fe(CO)_4$].

The dissociation constants of the free acids, determined in acetonitrile/water solutions (1/4 v/v) [5] are as expected lower than those in water, reported by Dippy [6]. The pK_a values correlate well with the Hammett σ values ($r = 0.99$)

TABLE 1

PHYSICAL PROPERTIES OF THE CINNAMIC ACIDS AND OF THEIR COMPLEXES WITH IRON TETRACARBONYL IN WATER/ACETONITRILE (4/1 v/v)

X	$XC_6H_4CH{=}CHCOOH$			$[Fe(CO)_4(\eta^2\text{-}C_6H_4XCH{=}CHCOOH)]$					
	λ_{max} (nm) [a]		pK_a	λ_{max} (nm) [a]		pK_a	ν(CO) (cm^{-1}) (acetonitrile)		
	acid	base		acid	base				
$3\text{-}NO_2$	265 (4.42)	261 (4.38)	4.38						
3-Cl	274 (4.31)	270 (4.25)	4.52	309 (4.08)	312 (3.97)	4.80	2098,	2026,	1992
4-Cl	284 (4.37)	275 (4.35)	4.62				2091,	2023,	1986
$3\text{-}OCH_3$	278 (4.29)	272 (4.22)	4.74	313 (4.11)	311 (4.05)	4.57	2094,	2021,	1987
H	278 (4.31)	272 (4.26)	4.78	308 (4.06)	311 (3.96)	4.90	2090,	2019,	1978
$4\text{-}CH_3$	288 (4.33)	277 (4.32)	4.92				2093,	2021,	1980
$4\text{-}OCH_3$	308 (4.31)	285 (4.27)	4.98	315 (4.13)	302 (4.09)	4.86	2094,	2021,	1987

[a] Log ϵ in parentheses.

and the $|\rho|$ value is higher than that obtained using Dippy's data, again as expected (ρ —0.64 and —0.48, respectively).

For the complexed acids, $[Fe(CO)_4(\eta^2\text{-}XC_6H_4CH{=}CHCOOH)]$, the dissociation constants are not much different from those of the free acids (Table 1). This is not surprising, since the strength of the complexed acid is influenced by two, opposing effects. Thus, $[Fe(CO)_4]$ can donate electrons, which is unfavourable for the dissociation of the acid [7—9], but at the same time the $[Fe(CO)_4]$ group on bonding to the olefinic bond disrupts the conjugation in the acid molecule. It is well known that olefinic systems bonded to transition metals are no longer planar [10], and this corresponds to a change in the hybridization of the olefinic bond from sp^2 to partial sp^3. The disruption of the conjugation has also been revealed by the UV spectra of $[(\eta^4\text{-polyene})Fe(CO)_3]$ systems [11], and $[(\eta^2\text{-olefin})Fe(CO_4]$ complexes show the same behaviour [12]. Since conjugation stabilizes the acid form [13], decrease in conjugation increases the dissociation constant of the acid. For acrylic acid, the electronic effect predominates because there is less delocalization in the acid [8].

It is further observed that the effect of the X substituents is smaller than in the free acids and do not satisfactorily correlate with the Hammett σ constants. A lowering of substituent effects on complexation has also been observed in other compounds, e.g. in $Cr(CO)_3$ complexes of phenol and aniline [3b,c]. In the present case, this behaviour also may be attributed to disruption of the conjugation on complex formation. This would lead to transmission of substituent effects mainly by induction, which, consequently decrease with increase in the distance of the $—CO_2H$ group from the substituent.

Experimental

(a) Preparation of $[Fe(CO)_4(\eta^2\text{-}XC_6H_4CH{=}CHCOOH)]$ complexes

$[Fe(CO)_4(\eta2\text{-}C_6H_5CH{=}CHCOOH)]$. 8 g of $[Fe_2(CO)_9]$ and 3.4 g of cinnamic acid (mole ratio 1/1.1) were allowed to react in deaerated benzene at 40°C. After ca 1 h, the $[Fe_2(CO)_9]$ in suspension had been consumed and a yellow precipitate was formed. The solid was filtered off and crystallized from MeOH; yield 80% (6 g). Anal. found: C, 49.70; H, 2.45. $C_{13}H_8FeO_6$ calcd.: C, 49.38; H, 2.55%. The compound decomposes without melting.

$[Fe(CO)_4(\eta^2\text{-}3\text{-}OMeC_6H_4CH{=}CHCOOH)]$. Similarly reaction of 5 g of $[Fe_2(CO)_9]$ and 2.6 g of ligand similarly at 35°C was complete after 2 h. The yellow precipitate was filtered off and crystallized from MeOH; yield 73% (3.5 g). Anal. found: C, 48.50; H, 2.91. $C_{14}H_{10}FeO_7$ calcd.: C, 48.57; H, 2.91%. The yellow solid decomposed without melting.

$[Fe(CO)_4(\eta^2\text{-}4\text{-}OMeC_6H_4CH{=}CHCOOH)]$. Similarly, reaction of 5 g of $[Fe_2(CO)_9]$ and 2.5 g of ligand (mole ratio 1/1.1) at 35°C was completed in 3 h. The solution was evaporated to dryness and the yellow solid (3.5 g, yield 65%) crystallized from MeOH. Anal. found: C, 48.21; H, 3.03. $C_{14}H_{10}FeO_7$ calcd.: C, 48.57; H, 2.91%. The solid decomposed without melting.

$[Fe(CO)_4(\eta^2\text{-}4\text{-}MeC_6H_4CH{=}CHCOOH)]$. Similarly, reaction of 5 g of $[Fe_2(CO)_9]$ and 2.5 g of ligand (mole ratio 1/1.1) at 35°C was complete in 1.5 h and the yellow precipitate (3.5 g, yield 78%) was crystallized from MeOH. Anal. found: C, 51.23; H, 3.23. $C_{14}H_{10}FeO_6$ calcd.: C, 50.92; H, 3.06%. The yellow solid decomposed without melting.

$[Fe(CO)_4(\eta^2\text{-}3\text{-}ClC_6H_4CH{=}CHCOOH)]$. 5 g of $[Fe_2(CO)_9]$ and 2.8 g of ligand were allowed to react in suspension in deaerated benzene at 40°C for 2 h. A slightly soluble yellow compound formed (3 g, yield 67%); it was filtered off and crystallized from MeOH. Anal. found C, 45.30; H, 2.21. $C_{13}H_7ClFeO_6$ calcd.: C, 44.53; H, 2.02%. The solid decomposed without melting.

$[Fe(CO)_4(\eta^2\text{-}4\text{-}ClC_6H_4CH{=}CHCOOH)]$. Since the ligand is only slightly soluble in benzene, 1.7 g of it were dissolved in deaerated benzene containing about 10% of MeOH, and 3.1 g of $[Fe_2(CO)_9]$ added. After 3 h at 35°C the solid was filtered off, dried, and recrystallized from MeOH. Anal. found: C, 45.09; H, 1.95. $C_{13}H_7ClFeO_6$ calcd.: C, 44.53; H, 2.02%.

$[Fe(CO)_4(\eta^2\text{-}3\text{-}NO_2C_6H_4CH{=}CHCOOH)]$ and $[Fe(CO)_4(\eta^2\text{-}4\text{-}NO_2C_6H_4CH{=}CHCOOH)]$. Because of the low solubility of both reactants and products, attempts to prepare these derivatives were unsuccessful. Evidence that they form was obtained from the IR spectra in Nujol in the carbonyl stretching region.

IR spectra were recorded on a Perkin—Elmer 521 spectrophotometer. CO stretching bands are listed in Table 1.

(b) Dissociation constants

pK_a values were determined by absorption spectrophotometry at 25°C; Britton buffers were used from pH 8 to pH 2, and HCl solutions for pH 1. Solute concentrations were of the order of 2×10^{-5} *M*. A Sargent PXB pH-meter with a glass electrode was employed. Absorption spectra were registered on an Optica CF4-DR double beam spectrophotometer and a DU-2 spectrophotometer.

Because of the sensitivity to air and light of the complexes in solution, the dissolution and the transfer to the cell were done in a nitrogen filled dry-box, in the dark. The stability of the complexes was confirmed by noting the spectra were unchanged during the experimental measurements.

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