Lewis Acidity of Tris(acetylacetonate) iron (III) Interactions with some Phosphine Derivatives in Methylene Chloride Solutions

ALI MUHAMMAD
Institute of Chemistry, University of the Punjab,
Quaid-e- Azam Campus, Lahore-54590, Pakistan

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Summary: The interactions between iron(III) acetylacetonate and a number of phosphine derivatives in methylene chloride were studied at 25°C by measuring the absorbances of the solutions at 430 nm. The absorbances were used to calculated equilibrium concentrations of the species in the solutions and then to evaluate equilibrium constants of these interactions. The equilibrium constant values indicate the following trend in the basic strength of the 1:1 adducts formed between phosphine derivatives and iron(III) acetylacetonate: $(C_2H_5)_3P > (ClC_6H_4)_3P > (C_6H_5)_3P > (C_6H_5)_2(CH_3O)P > C_6H_5(CH_3)_2P$. The formation of the above adducts is also supported by NMR study.

Introduction

The role of organometallic compounds is well established as catalysts [1,2] for the preparation of many useful organic compounds. For a particular system, the catalytic activity depends upon the electron accepting or electron donating properties of the catalysing substance. The transition metal compounds, behave by virtue of the availability [2,3] of incompletely filled d orbitals, as Lewis acids. For example, complexes of iron, copper and nickel have been reported [3-6] to show interactions with several donors e.g., ketones, heterocyclic nitrogen bases and phosphine derivatives. In transition metal organometallic compounds, nucleophilic attack has been proclaimed [7-9] to take place at the transition metal atom. In such behaviour, the coordination number of the metal atom is increased as the added species interact as a Lewis base.

In a recent work [10] it has been shown that iron acetylacetonate behaved as a Lewis base. It reacts with different MX_n type Lewis acids and strength of such Lewis acids has been compared by the acid-base interactions. In the present work, iron(III) acetylacetonate is shown to have properties of an electrophile. Its strength as a Lewis acid is not known. This paper presents the results of the interactions between iron(III) acetylacetonate and five phosphine derivatives to indicate their quantitative Lewis acid-base strength.

The phosphine derivatives, being electron donor molecules, interact with iron(III) acetylacetonate to form 1:1 adducts in methylene chloride solution. In general, the interaction may be represented as:

$$R_3P: + Fe(III)acac)_3 \xrightleftharpoons{K} R_3P: Fe(III)\,(acac)_3 \ldots..(i)$$

For the equilibrium (i)

$$pK = \log [R_3P{:}Fe(III)(acac)_3]/[R_3P][Fe(III)(acac)_3] \text{ ----} \qquad (ii)$$

Results and Discussion

Iron(III) acetylacetonate shows [11] spin forbidden transitions in the visible region at wave length 471 ($\log \varepsilon = 3.51$) and 352 nm ($\log \varepsilon = 3.52$) in absolute alcohol. In methylene chloride, iron(III) acetylacetonate is observed to show these transitions at λ_{max} 430 ($\log \varepsilon = 3.57$) and 353 nm ($\log \varepsilon = 3.58$) correspondingly.

Fig. 1 shows the UV-visible spectra of the solution of iron(III) acetylacetonate in methylene chloride (curve 1) and those of the solutions of the mixtures of different concentration of iron(III) acetylacetonate and $(C_2H_5)_3P$ in the same solvent (curves 2-8). By comparing these curves, it is concluded that the absorbances of the solution of iron(III) acetylacetonate in methylene chloride at two maxima i.e., 430 and 353 nm decrease on adding $(C_2H_5)_3P$. From the absorbance values at 430 nm, the equilibrium concentrations of the 1:1 adduct formed are determined. Knowing the stoichiometric concentrations of the phosphine derivative and the acetylacetonate, equilibrium con-

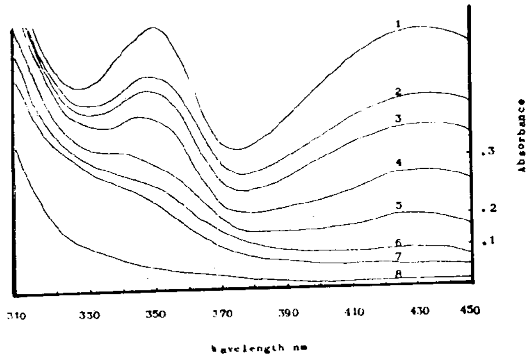

Fig. 1: UV absorption spectra of iron(III) acetylacetonate solution (1.69 x 10^{-4}M) in methylene chloride containing different conc. of triethylphosphine; (1) 0.00 (2) 0.01 (3) 0.02 (4) 0.035 (5) 0.030 (6) 0.76 (7) 0.10 (8) 0.207M.

centrations of the adduct and other species involved in eq. (i), are computed. Applying equation (ii), consistent values of equilibrium constants are obtained. The pK values, thus determined for triethylphosphine -Fe(III) $(acac)_3$ interactions are given in Table 1.

The experiments repeated on the same lines as for triphenylphosphine interactions with Fe(III)$(acac)_3$ gave consistent values for other phosphine derivatives. The pK values obtained for the different phosphine derivatives are given in Table 2.

The phosphine derivatives are nucleophiles because of the presence of lone pair of electrons on the phosphorus atom. The phosphorus atom differs from other donor atoms like nitrogen by the presence of empty d-orbitals possessing fairly low energy. If the metal atom, that receives the lone pair of electrons from the phosphorus atom already has electron in its orbitals having same symmetry, back donation will add strength to the $P \rightleftharpoons M$ bond. The intrinsic acidity of the metal atom is increased. When halogen, alkoxy or phenyl group is bonded to the phosphorus atom, the phosphine derivative shows [12] a strong tendency to go into five co-ordinate state. The donor character of the filled d-oribitals of a transition metal atom, is evident from the changes in the spectrum of iron(III) acetylacetonate on adding a phosphine derivatives. Thus electrons involved in the electron transition, as shown by absorption of iron(III) acetylacetonate in the visible region, are no more available on the iron atom on adduct formation.

The pK values determined for the various phosphine derivatives are consistent. Hence the stoichiometry of the adducts formed in solution, is 1:1. Graddon and Siddiqui have also shown [6] the stoichiometry of some phosphine adducts with transition metal complexes is 1:1 in acetonitrile solutions. Towards iron(III) acetylacetonate acting as Lewis acid, the basic strength of the phosphine derivatives is given in the following sequence:

$Et_3P > (p\text{-}ClC_6H_4)_3P > Ph_3P > Ph_2POCH_3 > PhP(CH_3)_2$.

Their relative quantitative basicities are in the ratio of 18.2:4.0:3.3:1.3:1. Thus triethyl phosphine forms an adduct which is about eighteen times more stable as compared with the least basic, dimethylphenylphosphine in the above series (cf. basicity [6] of $Bu_3P > Ph_3P$). It is not possible to correlate the basicity of the phosphine derivatives with the electron donating or electrophilic groups.

Table 1: Interaction of Iron(III) acetylacetonate with triethyl phosphine in methylene chloride solutions at 25°C.
$[Fe(III)(acac)_3]_{stoich} = 1.60 \times 10^{-4}$M: $[(C_2H_5)_3P]_{soich} = 0.01\text{-}0.207$ M
Calculation made at λ_{max} at 430 nm for the Fe(III)$(acac)_3$ absorption bond.
$\varepsilon_{430} = 3.698 \times 10^3$

No.	$[(C_2H_5)_3P]_{stoich.}$	Absorbance at 430 nm	$[Fe(III)(acac)_3]_{eq}$	$[C_2H_5)_3P]_{eq}$	$[Adduct]_{eq}$	pK
	M x 10^2		M X 10^4	M X 10^2	M X 10^4	
1.	0.00	0.625	1.69	-	-	-
2.	2.00	0.430	1.16	0.995	0.53	-1.66
3.	2.00	0.330	0.89	1.992	0.80	-1.65
4.	3.50	0.240	0.65	3.489	1.04	-1.66
5.	5.00	0.190	0.514	4.988	1.176	-1.66

Average pK value = - 1.65 ± .01

Table 2: pK values for the interactions of iron(III) acetylacetonate with phosphine derivatives in methylene chloride at 25 ± 1°C.

$[Fe(III)(acac)_3] = 1.69 \times 10^{-4}$ [Base] = .01 - .20 M

No.	Phosphine derivative	pK value ± 0.02
1.	Triethyl-	-1.65
2.	Tris p-chlorophenyl-	-0.99
3.	Triphenyl-	-0.91
4.	Diphenylmethoxy-	-0.49
5.	Dimethylphenyl-	-0.39

The presence of a halo or methoxy group has little effect upon the nucleophilicity of the phosphine derivative. The stability of such adducts has been explained [13] to depend largely upon the enthalpies of formation. Thus, stability of the P-M bond is dependent upon the strength of the bond. The $d\pi \longrightarrow d\pi$ back acceptance plays a major role to determine the strength of the P-M bond. Hence the nucleophilic character of the phosphine derivatives is overcome by the electrophilic acceptance which strengthens the transition metal-phosphine bond.

The NMR spectra

In order to confirm the above findings, arrived at by the UV work, it was thought to study the NMR spectra of iron(III) acetylacetonate and its mixture with diphenylmethylphosphine in methylene chloride solution. The spectra were recorded on Varian EM-390 90 MHz NMR spectrometer. On interaction of a Lewis base, the chemical shifts of protons located near the donor atom, can be markedly altered [14] on co-ordination of the electron pair. The protons, in iron(III) acetylacetonate, are present in an environment of high electron shielding. Therefore, its proton resonance is observed at -17 ppm as a broad band as shown in Fig. 2a. On addition of diphenylmethylphosphine, electron donation to the iron atom would increase the electron density on the iron complex and the acetylacetone ligand protons resonance will be expected to shift to the higher field. However, back donation to phosphorus empty d-orbitals will show a downfield shift of proton resonance for iron(III) acetylacetonate. On adduct formation, the protons of the iron complex resonate at -0.7 ppm as shown in Fig. 2b. A little deshielding effect is noticed for the methyl hydrogens of the phosphine derivative on phosphorus to metal bond formation. It is conceivable that strengthening of P-M bond (due to back donation) makes the metal ligand bonds weaker. Therefore, the ligand protons resonate in the low field.

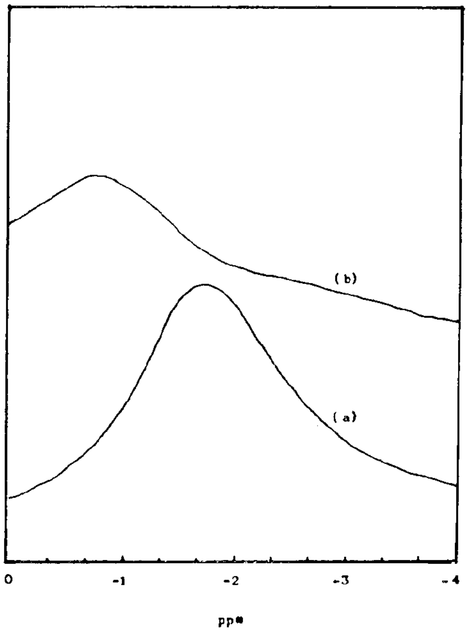

Fig.2: ^{1}H-NMR spectra of (a) $Fe(III)(acac)_3$ and (b) $Fe(III)(acac)_3 + Ph_2PCH_3$ in methylene chloride solutions.

Experimental

Iron(III) acetylacetonate and the phosphine derivatives were obtained from Fluka. They were used without further purification. The phosphine derivatives were sealed and kept under refrigeration. Methylene chloride, used as solvent, was refluxed with calcium hydride and distilled twice and kept over dried molecular sieve. The solvent and chemicals were kept in a dry box and all solutions were made in a dry atmosphere. On adding phosphine derivative solutions to iron(III) acetylacetonate solution, the spectra of the resulting solutions were measured using SP8-400 UV/VIS Pye-Unicam spectrophotometer.

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