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Equilibrium Studies of the Reactions of Tricarbonyl (2-methoxycyclohexadienyl) Iron (II) Cation with Some Amine Nucleophiles

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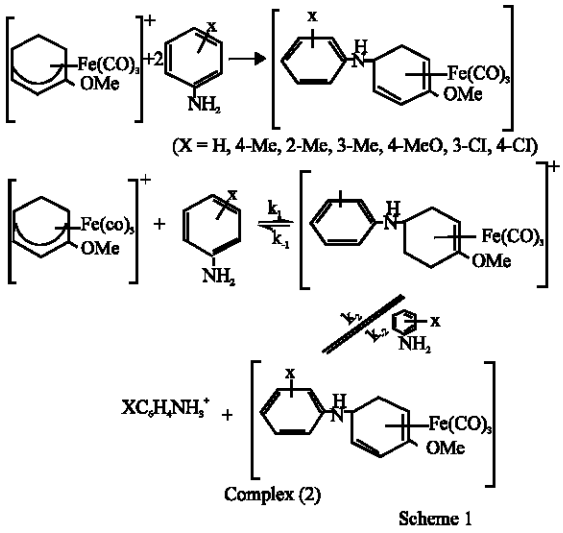
Abstract: The equilibrium study of the reactions of [(1-5-η-2 $MeOC_6H_6$) Fe $(CO)_3$]BF_4 with 4-dimethylaminopyridine, 2-aminopyrimidine and P-toluidine was studied in nitromethane at room temperature spectrophotometrically. The results show that the rate of reaction is dependent on the basicity of nucleophiles with the rate of reaction decreasing in the order 4-dimethylaminopyridine > 2-aminopyrimidine > P-toluidine. Our findings also indicate that the forward reactions are being favored than the reverse dissociation reactions since K_{eqm}>1 in each case.

Key words: Tricarbonyl (2-methoxycyclohexadienyl) Iron (II) Cation, amine nucleophiles, equilibrium study, basicity

INTRODUCTION

The influence of nucleophile basicity, steric and electronic nature of the co-ordinated organic group in the reactions of amines (Kane-Maguire *et al*., 1981a; Odiaka and Kane-Maguire, 1981; Kane-Maguire *et al*., 1981b; Odiaka, 1986, 1988, 1989a, 1989b), amides (Odiaka and Okogun, 1985), activated arenes (John and Kane-Maguire, 1979; Bonner *et al*., 1977), tertiary phosphines (Boman, 1978) and aryltrimethyl-silanes and stannanes (Odiaka, 1985) with organometallics of the type [(η^5-dienyl) Fe $(CO)_3$] BF_4 (Complex 1, where dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_6) to form new 1,3-diene organometallics have been well established. The stepwise process of the reaction of [Fe(η^5-C_6H_6MeO-2)$(CO)_3$]BF_4 with P-toluidine and some other anilines (X = H, 2-Me, 3-Me, 2-Cl, 3-Cl, 4-Cl, 4-OMe and 4-NO_2) in CH_3CN have provided quantitative information on the importance of basicity and steric factors in controlling amine nucleophilicity towards co-ordinatd π-hydrocarbons (Kane-Maguire *et al*., 1981a, b; Odiaka and Kane-Maguire, 1981). The products are pyridinium adducts of tricarbonyl (2methoxycyclohexa-1,3-diene) Iron. This reaction is generally represented as Eq. 1 below and the mechanism of reaction is also represented as scheme 1.

The reaction initially appeared to proceed to completion in CH_3CN fpr the more basic anilines (X = 4-Me, 4-MeO) under the kinetic conditions [Fe] = 1.5×10^{-3} moldm^{-3}; [$XC_6H_4NH_2$] $\geq$ 2×10^{-2} moldm^{-3}, while K_{obs} = K_1



Scheme 1

[amine]. The products have been characterized by analyses, ^{1}Hn.m.r, I.R and field-desorption mass spectroscopy (Kane-Maguire *et al*., 1981a, b; Odiaka and Kane-Maguire, 1981). A stopped-flow kinetic study of the reaction in CH_3CN yield the general rate law,

Rate = K [Fe] [$XC_6H_4NH_2$]. However, for the equilibrium reactions of the remaining other basic amines the two-term expression.

K_{obs} = K_1[amine] + K_{-1}[H^+]/([H^+] + K_2K_{-2}) is indicated even at the highest nucleophile concentrations employed (Kane-Maguire *et al*., 1981b). And K_2 >> K_1, K_{-1}, K_{-2}.

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Detailed equilibrium constant studies of the over-all reactions of complex (1) with these amine nucleophiles have also been carried out using the method of Kane-Maguire (1981a, b) and Odiaka and Kane-Maguire (1971). In order to enrich our understanding of the dynamics of equilibrium studies in organometallic systems of these types, we have made another detailed equilibrium study of these over-all reactions of [(1-5-η- 2 $MeOC_6H_6$) Fe $(CO)_3]^+$ with P-toluidine, 4-dimethylaminopyridine and 2-aminopyrimidine basing all equilibrium constant calculations on the recorded U.V. spectra and not the I.R. spectra.

Recent study has revealed that pyridine derivatives stimulate phosphatidylcholine (major lipid component of the cell membrane) secretion (Kai *et al*., 1996). Derivatives of P-toluidine have also been reported as suitable antiallergenic, antiasthmatic or cardiotonic drugs, central nervous system stimulant and diuretics (Jacobson *et al*., 1986). Also brominated derivatives of 2-aminopyrimidine have been discovered to prevent cell proliferation and induce apoptosis, a demonstration of their ability to enter cells and to interfere with the activity of kinases important for cell division and cell death (Marie *et al*., 2004). Advances in organometallics has equally revealed that an Irontricarbonyl complex that contains a 2-pyrone motif liberates CO invitro and exerts pharmacological effects like vasorelaxation and inhibition of inflammatory responses, which are typical of CO gas (Philip *et al*., 2006).

More compounds could be synthesized by reacting complex (1) with more of these amine nucleophile derivatives and these newly synthesized compounds are also expected to be of great synthetic and biopotencial importance. The equilibrium study of such organometallic systems involving complex (1) seem interesting even with UV-Visible spectroscopy.

MATERIALS AND METHODS

The organometallic complex [(1-5-η- 2 $MeOC_6H_6$) Fe $(CO)_3]BF_4$ was synthesized and purified using published procedures (Birch *et al*., 1968). All the amines used were purchased in the purest grades available (Aldrich). Nitromethane was distilled in bulk and dried over molecular sieves (grade 3A) prior to use. The substituted diene product (2) from the reaction of complex (1) with P-toluidine has been isolated and fully characterized elsewhere (Kane-Maguire *et al*., 1981a, b; Odiaka and Kane-Maguire, 1971).

Organometallic system: Five milliliter of 1.5×10^{-3}M complex solution in CH_3NO_2 was pipetted into a flask. Five milliliter of 2.0×10^{-1}M P-toluidine solution was also pipetted and added to the flask. Both were mixed at room temperature for 60 sec. A unicam Aurora for Helios Scan software v.1.1 UV-Visible spectrophotometer was used to obtain the absorbance spectrum. The spectrum was first obtained for the complex alone, then for the amine nucleophile alone and finally for the product. This procedure was repeated separately using 2-aminopyrimidine, then P-toluidine (but 2.0×10^{-1}M P-toluidine was used).

Equilibrium studies: The equilibrium constant for each organometallic system was studied and calculated according to the method of Kane-Maguire (1971) (Birch *et al*., 1968; Kane-Maguire *et al*., 1981a, b) with little modification using U.V. Equilibrium constants for the over-all reactions of the organometallic complex [(1-5-η-2 $MeOC_6H_6$) Fe $(CO)_3]$ BF_4 with each of the amine nucleophiles were determined by dissolving the appropriate dienyl salt in nitromethane solution (25°C) of the amines of varying concentrations and recording the U.V. spectra in the region 370-420 nm. The equilibrium concentrations of the unreacted [(1-5-η- 2 $MeOC_6H_6$) Fe $(CO)_3]^+$ ions were calculated from their known (Kai *et al*., 1996) absorption co-efficient. From the known starting concentrations, the equilibrium concentrations of the products could then be estimated, allowing calculation of the equilibrium constants K_{eqm} using (2) below:

$$K_{eqm} = \frac{[\text{Product at Equilibrium}]}{[\text{Complex}]_{eqm} \times [\text{Amine}]_{eqm}} \quad (2)$$

The equation for the over-all reactions[1] is (3) below, except with pyridines where only one molecule of the nucleophile is reacting (Odiaka, 1996).

$$[(\eta^5\text{-dienyl}) \text{ Fe } (CO)_3] + 2RNH_2 \rightleftharpoons [(\eta^4\text{-diene NHR}) \text{ Fe } (CO)_3] + RNH_3^+ \quad (3)$$

Thus Eq. 2 above will become Eq. 4 where K_{eqm} can easily be calculated out

$$K_{eqm} = \frac{[(\eta^4\text{-diene NHR}) \text{ Fe } (CO)_3] [RNH_3^+]}{[(\eta^5\text{-dienyl}) \text{ Fe } (CO)_3] [RNH_2]^2} \quad (4)$$

RESULTS AND DISCUSSION

The calculated equilibrium constants for the addition of these amine nucleophiles to the dienyl ring of [(1-5-η- 2 $MeOC_6H_6$) Fe $(CO)_3]BF_4$ at room temperature in CH_3NO_2 is collected in Table 1.

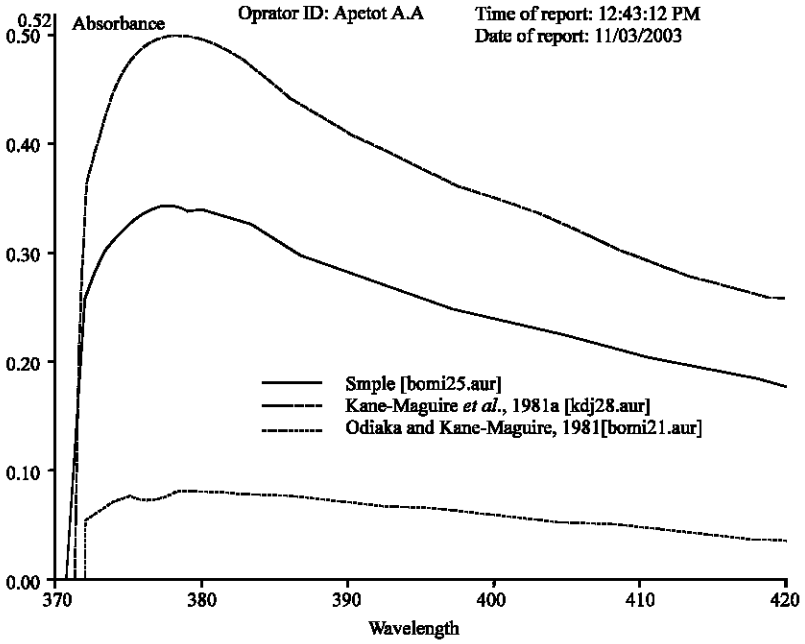
Considering the pK_a values of the amine nucleophiles in Table 2, the basicity of these nucleophiles would decrease in the order Pyridine > P-toluidine > Pyrimidine. The two methyl groups in 4-dimethylaminopyridine would release electrons to the nitrogen at para-position of the pyridine ring. Thus stabilizing the ion formed relative to the unsubstituted pyridine and also activating the aromatic ring towards electrophilic substitution. Therefore, the basicity of 4-dimethylaminopyridine would be the most reactive towards $[(1\text{-}5\text{-}\eta\text{-}\ 2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ cation. Hence the calculated K_{eqm} value of 98.0dm^3mol^{-1} recorded for 4-dimethylaminopyridine is the highest K_{eqm} value in Table 1. This is consistent with nucleophilicity. It shows that it is the most reactive. P-toluidine is expected to be less reactive than 4-dimethylaminopyridine. The calculated K_{eqm} of 67.0dm^3mol^{-1} for its reaction with $[(1\text{-}5\text{-}\eta\text{-}2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ cation is consistent with expectations. The amino substituent on position 2 of 2-aminopyrimidine would release electrons to the pyrimidine ring, this stabilizes the ion formed relative to the unsubstituted pyrimidine, thus increasing the basicity. It is still expected that it will be the least reactive towards

Table 1: Equilibrium constants for the addition of some amine nucleophiles to $[(1\text{-}5\text{-}\eta\text{-}\ 2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ cation in CH_3NO_2 at 25°C

Amine	K_{eqm} (dm^3mol^{-1})
P-toluidine	67.0
2-aminopyrimidine	73.0
4-dimethylaminopyridine	98.0

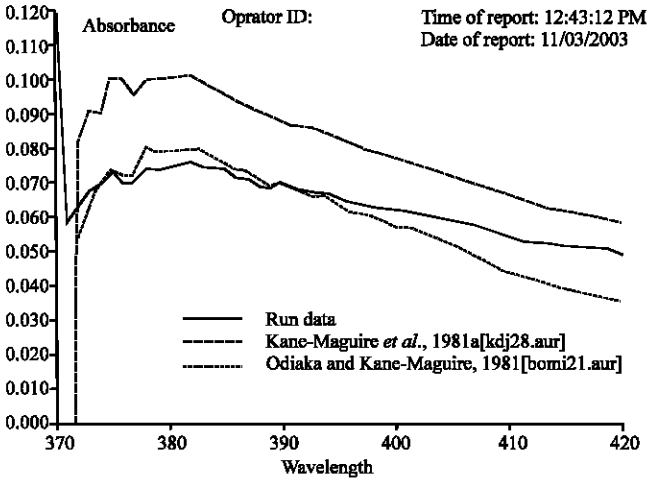
Table 2: Strengths of conjugate acids of some amine nucleophiles in aqueous solution at 25°CN

Ncleophile	K_b	pK_b	pK_a
Pyridine	1.7×10^{-9}	8.77	5.23
P-toluidine	1.0×10^{-9}	8.90	5.10
Pyrimidine	2.0×10^{-3}	12.70	1.30



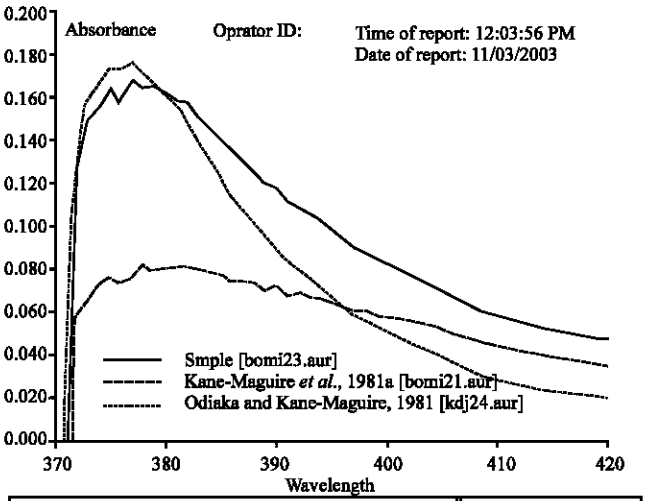
Method		Peak table	
Start: 370	Graph high: . 52		Wavelength Abs
Stop: 420	Graph low: 0	1	379 0.338
Interval: 1	Peak pick mode: Manuel	2	380 0.339
Mode: Absorbance	Bandwidth: 2nm	3	381 0.335
Sample ID: Toluidine		4	
		5	
Time of scan: 12:39:49		6	
Date of scan: 11/03/20		7	
		8	
		9	
		10	

Fig. 1: UV Spectra of the reaction of $[(1\text{-}5\text{-}\eta\text{-}\ 2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ Cation with P-toluidine showing the various absorption co-efficient, Note: Sample-Complex alone; Kane-Maguire *et al.*, 1981a-Amine alone; Odiake and Kane-Maguire, 1968-Complex + Amine



Method		Peak table		
Start: 370	Graph high: .12		Wavelength	Abs
Stop: 420	Graph low: 0	1	379	0.074
Interval: 1	Peak pick mode: Manuel	2	380	0.074
Mode: Absorbance	Bandwidth: 2nm	3	381	0.076
Sample ID: Pyrmidine		4		
Time of scan: 12:26:59		5		
Date of scan: 11/03/20		6		
		7		
		8		
		9		
		10		

Fig. 2: UV Spectra of $[(1\text{-}5\text{-}\eta\text{-}\ 2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ Cation with 2-aminopyrimidine showing the various absorption co-efficient, Note: RUN DATA-Complex alone; Kane-Maguire *et al.*, 1981a-Amine alone; Odiake and Kane-Maguire, 1968-Complex + Amine



Method		Peak table		
Start: 370	Graph high: .2		Wavelength	Abs
Stop: 420	Graph low: 0	1	379	0.165
Interval: 1	Peak pick mode: Manuel	2	380	0.162
Mode: Absorbance	Bandwidth: 2nm	3	381	0.158
Sample ID: Pyridine		4		
Time of scan: 12:01:06		5		
Date of scan: 11/03/20		6		
		7		
		8		
		9		
		10		

Fig. 3: UV spectra of the reaction of $[(1\text{-}5\text{-}\eta\text{-}\ 2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ Cation with 4-dimethylaminopyridine showing the various absorption co-efficient, Note: Sample-Complex alone; Kane-Maguire *et al.*, 1981a-Amine alone; Odiake and Kane-Maguire, 1968-Complex + Amine

$[(1\text{-}5\text{-}\eta\text{-}2\ MeOC_6H_6)\ Fe\ (CO)_3]^+$ cation. But its K_{eqm} value of $73dm^3mol^{-1}$ is higher than that of P-toluidine of $67dm^3mol^{-1}$ (Fig. 1-3). The reason for this is not immediately identified, but could be due to solvent effect. Also, all the calculated equilibrium constants show that the forward reaction is more favourable than the reverse dissociation reaction in each case.

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