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Steric and electronic influences on the rate of addition of pyridines to the tricarbonyl(cycloheptadienyl) iron(II) cation

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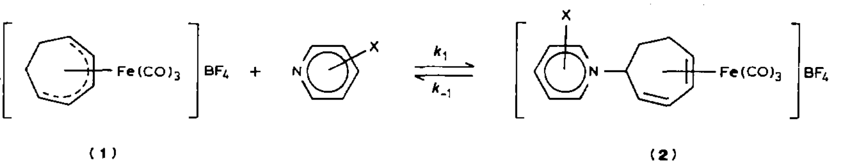
Abstract

Kinetic studies of the reversible addition of pyridines to the cation $[Fe(1\text{–}5\text{-}\eta\text{-}C_7H_9)(CO)_3]^+$ provide detailed information on the influence of steric and electronic factors on the nucleophilicity of amines towards coordinated organic substrates. Brönsted plots of log k_1 (forward rate constant) against the pK_a's of the amine conjugate acids demonstrate the dependence of rate on amine basicity and reveal that successive blocking of the 2- and 6-positions of pyridine by methyl (or formyl) groups leads to marked non-additive steric retardation.

Introduction

In earlier work we examined the addition of a wide variety of aromatic substrates to coordinated π-hydrocarbons of varying steric and electronic properties to form novel 1,3-diene organometallics [1–10]. Recently a study of the reactions between $[Fe(1\text{–}5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ (3) and X-substituted pyridines (X = H, 2-Me, 3-Me, 4-Me, 4-Ph, 2-Cl, 3-CN, 2,5-Me_2, 2,6-Me_2, 3,5-Me_2 or 2,4,6-Me_3) in MeCN revealed the importance of basicity and steric effects in controlling the amine nucleophilicity towards coordinated π-hydrocarbons; the reactions gave products of the type tricarbonyl(1–4-η-5-*exo*-*N*-pyridiniocyclohexa-1,3-diene)iron tetrafluoroborate in yields of 60–70% [11]. We report here the results of a kinetic study of the addition of pyridines to the cation $[Fe(1\text{–}5\text{-}\eta\text{-}C_7H_9)(CO)_3]^+$ (1) in MeCN (eq. 1, X = H, 2-Me, 2-CHO, 4-Ac, 2,4-Me_2, 2,5-Me_2, 2,6-Me_2, 3,4-Me_2, 3,5-Me_2 or 2,4,6-Me_3) designed to improve understanding of the mechanism and of the influence of steric



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and electronic properties of amine additions to coordinated π-hydrocarbons. This work examines the nucleophilicity of pyridines towards the C_6H_7 (3) and C_7H_9 (1) complexes and thus throws light not only on the relative electrophilities of these complexes but also on how a change in the nature of the coordinated π-hydrocarbon can influence the nature of the transition states in such systems.

Experimental

Materials

The complex **1** was synthesized and purified as previously described [12]. The pyridines were purchased (BDH or Aldrich) in the purest grade available and freshly distilled over KOH pellets before use. Acetonitrile (BDH) was distilled in bulk and stored over molecular sieves (size 3 Å) under dinitrogen.

Kinetic studies

The reactions (eq. 1) in MeCN were studied under pseudo-first-order conditions involving use of a large excess of the nucleophile ([Fe] = 1.5×10^{-3} mol dm^{-3}, [amine] = 0.01–1.0 mol dm^{-3}). The reactions were rapid and were monitored with a thermostatted (±0.1°C) stopped-flow spectrophotometer at a wavelength of 390 nm, where a large decrease in absorbance was observed. The reaction traces were recorded and analysed using a rapid data-capture system (Lombardi Scientific Ltd.) employing computer programs developed jointly with Lombardi (U.K.) Ltd. and described elsewhere [13]. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of $\log(A_t - A_\infty)$ against time which were linear for at least two half-lives. Each k_{obs} is the average from at least six separate runs, with an average reproducibility of ±3%. Second-order rate constants, k_1, were calculated by least-squares analysis of plots of k_{obs} against [amine]. Activation enthalpies were obtained from the slopes of Arrhenius plots of $\log k_1$ or $\log k_{-1}$ versus T^{-1}, calculated by a least-squares method. Entropies of activation were calculated from the second- and first-order rate constants, k_1 and k_{-1} respectively.

Results and discussion

Nature of the reactions

The nature of the reactions between the organometallic complex **1** and a wide variety of pyridines has been established by the isolation and characterisation of some of the pyridinium adducts (**2**; X = H, 2-Me, 2-Et, 2,6-Me_2 or 2,4,6-Me_3) and by in situ IR and ^1H NMR spectral studies of several others [5,11,14]. Their IR spectra showed two strong carbonyl bands at ca. 2055 and 1980 cm^{-1}. The same two ν(CO) bands were observed during the IR studies of reactions (1) using a large excess of the amine nucleophile, indicating the formation of the same tricarbonyl [1–4-η-5-*exo*-*N*-pyridiniocyclohepta-1,3-diene] iron complexes. In addition to the two strong ν(CO) bands at 2055 and 1980 cm^{-1}, these products (**2**) also exhibited the characteristic broad band at ca. 1060 cm^{-1} attributed to the BF_4^- anion. For each of the reactions of complex **1** with equimolar amounts of the appropriate amine nuocleophile, in situ IR studies showed the presence of ν(CO) bands at 2120 and 2065 cm^{-1} as well as those due to the products **2**, indicating that reactions (1) are reversible.

Kinetics and mechanism

Kinetic results for the addition of pyridine to cation **1** are collected in Table 1. Less extensive kinetic results for other substituted pyridines are summarised in Table 2. These results show close adherence to the second-order rate law (eq. 2),

$$\text{Rate} = k_1[\text{complex}][\text{amine}] + k_{-1}[\text{complex}]$$

$$k_{\text{obs}} = k_1[\text{amine}] + k_{-1} \qquad (2)$$

which is consistent with an equilibrium process. The values of k_{-1} for the substituted pyridines in Table 2 tend to zero, but should at higher temperature increase progressively (see Table 1 and ref. 5), as expected for a reversible process. Thus plots of k_{obs} against [amine] are linear with non-zero intercepts. The slopes of these plots give k_1, the second-order rate constant for direct addition to the dienyl ring of **1**, while the intercepts on the k_{obs} axis refer to k_{-1}, the first-order rate constant for the dissociation of the amine nucleophile from the pyridinium adducts **2**. The low $\Delta H_1^{\neq}$ value of 26.3 ± 0.6 kJ mol^{-1} and large negative $\Delta S_1^{\neq}$ value of -107 ± 2 J K^{-1} mol^{-1} found for the pyridine reaction (Table 3) are as expected for direct addition to the dienyl ring of **1**. On the other hand, the much larger $\Delta H^{\neq}_{-1}$ value of 103 ± 0.5 kJ mol^{-1} is as expected for bond cleavage in dissociation (k_{-1}), as is the positive $\Delta S^{\neq}_{-1}$ of $+100 \pm 1$ J K^{-1} mol^{-1} determined for the pyridine reaction.

Table 3 also compares the results of the reactions of pyridine and 2-ethylpyridine with complex **1** and shows a large negative $\Delta S^{\neq}_{-1}$ value of -97 ± 8 J K^{-1} mol^{-1} for the latter amine. Such large negative entropies of activation are common features in

Table 1

Kinetic data for reactions of $[\text{Fe(CO)}_3(1\text{-}5\text{-}\eta\text{-C}_7\text{H}_9)]\text{BF}_4$ with pyridine in CH_3CN ($[\text{Fe}] = 1.5 \times 10^{-3}$ mol dm^{-3})

T (°C)	$10^2[\text{NC}_5\text{H}_5]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_1 [a] (dm^3 mol^{-1} s^{-1})	k_{-1} [a] (s^{-1})
0.0	1.0	1.18		
0.0	2.0	2.35		
0.0	4.0	4.70		
0.0	8.0	9.29		
0.0	10.0	11.7	117(0.4)	0.019(0.02)
10.1	1.0	1.91		
10.1	2.0	3.92		
10.1	4.0	7.64		
10.1	8.0	15.2		
10.1	10.0	18.9	188(0.6)	0.092(0.04)
15.3	1.0	2.62		
15.3	2.0	5.23		
15.3	4.0	9.93		
15.3	8.0	19.7		
15.3	10.0	24.4	242(1)	0.243(0.06)
20.2	1.0	3.41		
20.2	2.0	6.50		
20.2	4.0	12.2		
20.2	8.0	24.3		
20.2	10.0	30.1	297(1)	0.464(0.07)

[a] Estimated by a least-squares fit to eq. 2, with estimated standard deviations.

the dissociative processes of amine additions to organometallics of the types **1** and **3** [5,9,14] and may be rationalised in terms of the "ordered transition state mechanism" [9]. At 0 °C, pyridine is 18 times as reactive as 2-ethylpyridine towards

Table 2

Kinetic data for reactions of $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_9)]BF_4$ with other pyridines in CH_3CN at 0 °C ($[Fe] = 1.5 \times 10^{-3}$ mol dm^{-3})

Nucleophile	10^2[Nucleophile] (mol dm^{-3})	k_{obs} (s^{-1})	k_1 [a] (dm^3 mol^{-1} s^{-1})	k_{-1} [a] (s^{-1})
$NC_5H_3Me_2$-3,5	1.0	3.59		
	2.0	7.43		
	4.0	16.1		
	8.0	33.2	425(2)	0.01(0.12)
$NC_5H_3Me_2$-3,4	1.0	3.99		
	2.0	7.56		
	4.0	14.1		
	6.0	21.8		
	8.0	29.1	359(4)	0.25(0.22)
$NC_5H_3Me_2$-2,4	1.0	0.424		
	2.0	0.910		
	4.0	1.74		
	8.0	3.51		
	10.0	4.38	43.8(0.2)	0.01(0.01)
$NC_5H_3Me_2$-2,5	1.0	0.383		
	2.0	0.746		
	4.0	1.59		
	8.0	3.20		
	10.0	3.98	40.2(0.2)	0.01(0.01)
NC_5H_4Ac-4	2.5	0.773		
	5.0	1.50		
	10.0	2.98		
	15.0	4.58		
	20.0	6.13	30.7(0.2)	0.01(0.03)
NC_5H_4Me-2	1.0	0.294		
	2.0	0.580		
	4.0	1.16		
	8.0	2.31		
	10.0	2.96	29.4(0.3)	0.01(0.02)
NC_5H_4CHO-2	2.5	0.250		
	5.0	0.519		
	10.0	1.08		
	15.0	1.66		
	20.0	2.20	11.2(0.06)	0.02(0.01)
$NC_5H_3Me_2$-2,6	10.0	0.281		
	20.0	0.635		
	40.0	1.34		
	50.0	1.70		
	100.0	3.41	3.48(0.02)	0.02(0.02)

[a] Estimated by a least-squares fit to eq. 2; estimated standard deviations are shown in parentheses.

Table 3

Activation parameters for addition of pyridine and 2-ethylpyridine [5] to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_9]BF_4$ in CH_3CN

Nucleophile	k_1(rel.)/ 0 °C	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H_{-1}^{\neq}$ (kJ mol^{-1})	$\Delta S_{-1}^{\neq}$ (J K^{-1} mol^{-1})
NC_5H_5	18	26.3(0.6)	−107(2)	103(0.5)	+100(1)
$NC_5H_4Et\text{-}2$	1	37.8(0.54)	−90(2)	48(2.2)	−97(8)

complex **1** (Table 3). This is almost certainly due to a higher enthalpy of activation for 2-ethylpyridine, associated with the steric influence of the ethyl substituent.

Influence of nucleophile basicity

The rate of addition of pyridines to complex **1** follows the sequence 3,5-$(Me)_2$ > 3,4-$(Me)_2$ > H > 2,4-$(Me)_2$ > 2,5-$(Me)_2$ > 4-Ac > 2-Me > 2-CHO > 2,4,6-$(Me)_3$ > 2,6-$(Me)_2$ (Tables 1,2,4). For the unhindered pyridines the reactivity decreases with decreasing basicity of the pyridine (Table 4). A Brönsted plot of log k_1 against the pK_a of the amine conjugate acid in H_2O [15] (Fig. 1) gave a slope, α, of 0.4 for addition of non-sterically crowded pyridines to **1**. This slope is very similar to the α value of ca. 0.5 found for amine addition to free carbonium ions [16], indicating a strong dependence of rate on amine basicity and suggesting, on the basis of the reasoning of Pearson et al. [17], that cation **1** is a 'hard' species. A similar plot [11] for addition of such unhindered pyridines to $[Fe(1\text{-}5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ (**3**) gave an α value of 1.0, indicating a much greater electrophilicity for complex **3** than for complex **1**. This much higher value also indicates the much greater accumulation of positive charge in the transition states of pyridine reactions with **3** than in their analogous reactions with complex **1**. The assignment of a 'hard' character to the dienyl rings of complexes **1** and **3** is consistent with their frequent representation as stabilised carbonium ions, and with the high positive charges shown by calculations [18] to reside on the ring carbons.

Table 4

Variation of rates with amine basicity for the reactions of pyridines with $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in CH_3CN at 0 °C

Amine	k_1 (dm^3 mol^{-1} s^{-1})	pK_a (H_2O) [a]
$NC_5H_3Me_2\text{-}3,5$	425	6.55
$NC_5H_3Me_2\text{-}3,4$	359	6.52
NC_5H_5	117	5.60
$NC_5H_3Me_2\text{-}2,4$	43.8	7.14
$NC_5H_3Me_2\text{-}2,5$	40.2	6.63
$NC_5H_4Ac\text{-}4$	30.7	3.70
$NC_5H_4Me\text{-}2$	29.4	6.41
$NC_5H_4CHO\text{-}2$	11.2	3.80
$NC_5H_3Me_2\text{-}2,6$	3.48	7.35
$NC_5H_2Me_3\text{-}2,4,6$	4.24 [b]	7.43

[a] Values from ref. 15a, except those for $NC_5H_4CHO\text{-}2$ and $NC_5H_2Me_3\text{-}2,4,6$ which are from ref. 15b.
[b] Value from ref. 11.

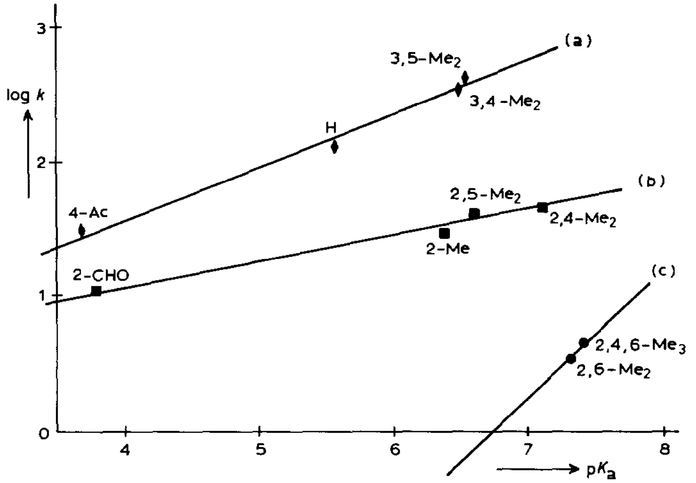

Fig. 1. Brönsted plots for the reactions of $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in CH_3CN at 0 °C with (a) unhindered pyridines; (b) pyridines with 2-Me or 2-CHO groups, and (c) pyridines with $2,6\text{-}Me_2$ groups.

Steric influence of nucleophile

The steric effects of pyridine additions to complex **1** are clearly evident from Fig. 1 and Table 5 ($NC_5H_5 > NC_5H_4Me\text{-}2 > NC_5H_4Et\text{-}2 > NC_5H_3(Me)_2\text{-}2,6$; relative rates 34/8/2/1). The three straight lines shown in Fig. 1 are plots of log k_1 against the pK_a of the amine conjugate acid for (a) unhindered pyridines, (b) pyridines bearing a methyl or formyl group at the 2-position, and (c) pyridines bearing methyl groups at both 2- and 6- positions. The distance of ca. 1.0 log units between graphs (a) and (b) indicates that there is a 10-fold rate decrease due to steric hindrance by a 2-methyl substituent in the pyridine nucleophile and similarly distance of ca. 3 between graphs (a) and (c) suggests ca. a 1000-fold rate decrease due to steric effects when both the 2- and 6-positions bear methyl groups. These results confirm the importance of steric effects in reactions (1) and the distance of ca. 1.5 log units between graphs (b) and (c) demonstrates that the steric effects of successive addition of methyl groups to pyridine (2-Me; $2,6\text{-}(Me)_2$) are non-additive; the combined steric effect of methyl groups at the 2,6-positions on the entropy of the transition state is more than twice as large as that of one methyl group. With complex **3**, the presence of methyl groups at the 2- and 2,6-positions of the pyridine nitrogen caused a 10-fold and 10000-fold rate decreases, respectively [11]. The more pro-

Table 5

Steric effects on rates for addition of substituted pyridines to $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_7H_9)]BF_4$ in CH_3CN at 0 °C

Amine	k_1 ($dm^3\ mol^{-1}\ s^{-1}$)	k_1 (rel.)
NC_5H_5	117	34
$NC_5H_4Me\text{-}2$	29.4	8
$NC_5H_4Et\text{-}2$ [a]	6.54	2
$NC_5H_3Me_2\text{-}2,6$	3.48	1

[a] Rate constant from ref. 5.

nounced steric influence in pyridine additions to complex **3** than in those to complex **1** is not surprising since a more reactive cationic complex is expected to exhibit much greater variation in rate for attack by nucleophiles [19]. The lower reactivity of $[Fe(1-5-\eta-C_7H_9)(CO)_3]^+$ (**1**) than of the parent cation $[Fe(1-5-\eta-C_6H_7(CO)_3]^+$ (**3**) is readily accounted for in terms of the additional steric hindrance caused by the extra methylene group in **1** if it is assumed that the pyridines approach from above the dienyl rings.

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