

Steric and Electronic Influences on the Rate of Addition of Anilines to the Tricarbonyl (Cyclohexadienyl) Iron(II) Cation

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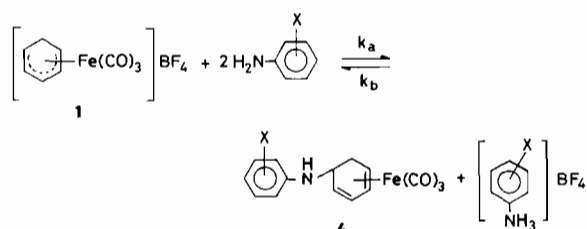
Abstract

Kinetic studies of the reversible addition of anilines to the cation $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7)(\text{CO})_3]^+$ (**1**) provide detailed information on the influence of steric and electronic factors on the nucleophilicity of amines towards coordinated organic substrates. For the unhindered anilines, a Brønsted plot of $\log k$ (forward rate constant) against the $\text{p}K_{\text{a}}$ values of the amine conjugate acids has a high slope of 1, indicating a very strong dependence of rate on amine basicity. A Hammett plot for this reaction gives a slope of -3.23 indicating significant bond formation and a considerable build-up of positive charge on the aniline nitrogen atom in the transition state. Anilines bearing substituents at the 2-position exhibit a considerably smaller steric retardation of k than in the analogous reactions of pyridines with **1**.

Introduction

In earlier work we examined how variations in the steric and electronic properties of coordinated organic molecules affect their reactivity towards a wide variety of aromatic substrates such as amines [1–7], amides [8], tertiary phosphines [9–12], activated arenes [13–15] and aryltrimethyl-silanes and -stannanes [16–17]. Some progress has also been made in establishing the influence of nucleophile basicity and its steric nature on the rate and mechanism of addition to coordinated organic molecules, e.g. anilines [3] and pyridines [4, 18]. Recently a study of the reactions between $[\text{Fe}(1\text{-}5\text{-}\eta\text{-}2\text{-Me-OC}_6\text{H}_6)(\text{CO})_3]^+$ (**2**) and X-substituted anilines [3] (X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl or 4-OMe) and of 4-chloroaniline [19] with **1**, **2** and $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_7\text{H}_9)(\text{CO})_3]^+$ (**3**) in MeCN revealed the importance of basicity and steric effects in controlling the amine nucleophilicity towards coordinated π -hydrocarbons [3] and threw some light on the nature of the transition state in these systems [19]. The reactions of anilines with complex **3** have also been studied recently [20]. These aniline reactions gave neutral products of the type tricarbonyl (1,4- η -5-exo-*N*-

anilincyclohexa- (or cyclohepta-) 1,3-diene) iron in high yields. We report here the results of a kinetic study of the addition of anilines to the cation $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7)(\text{CO})_3]^+$ (**1**) in MeCN (eqn. (1), X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-Cl, 2-OMe, 3-Ome, 4-OMe, 3,4-(Me)₂ or 2,6-(Me)₂) designed to improve



understanding of the mechanism and of the influence of steric and electronic properties on amine additions to coordinated π -hydrocarbons. This work examines the nucleophilicity of anilines towards the organometallic **1**, **2** and **3** and thus throws light not only on the relative electrophilicities of these complexes but also on the relationship between the nature of the coordinated organic group and the degree of positive charge formation in the transition states of these systems.

Experimental

Materials

Complex **1** was synthesized and purified as previously described [21]. The anilines were purchased (BDH or Aldrich) in the purest grade available. The liquids were freshly distilled under a dinitrogen atmosphere and dried over molecular sieves (size 3 Å) prior to use. Acetonitrile (BDH) was distilled in bulk and stored over molecular sieves (size 3 Å) under dinitrogen.

Kinetic Studies

The reactions (eqn. (1)) in MeCN were studied under pseudo-first-order conditions involving use of a large excess of the nucleophile ($[\text{Fe}] = 1.5 \times 10^{-3}$ mol dm⁻³, $[\text{amine}] = 0.01\text{--}0.20$ mol dm⁻³). The reactions of 4-methoxyaniline and 3,4-dimethyl-

aniline with complex **1** in CH₃CN were studied under equimolar conditions ([Fe] = [amine] = 1.5 × 10⁻³ mol dm⁻³) and obeyed the kinetic expression (2), where *a* represents the initial concentration of complex **1**, and *x* the concentration of the product formed at time, *t*. The reactions (1) were rapid

$$\frac{x}{a(a-x)} = kt \quad (2)$$

and were monitored with a thermostated (±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 [22]. Pseudo-first-order rate constants, *k*_{obs}, were calculated from the slopes of log(*A*_t - *A*_∞) against time which were linear for at least two half-lives. Each *k*_{obs} value is the average from at least six separate runs, with an average reproducibility of ±3%. Second-order rate constants, *k*_a, were calculated by least-squares analysis of plots of *k*_{obs} against [amine]. For the equimolar runs, the second-order rate constants, *k*_a were derived from the slopes of plots of *x/a(a-x)* against time which were linear for at least 65% completion of reaction. Each kinetic run was carried out in quadruplicate, the reproducibility of the rate constants being ±4%.

Results and Discussion

Nature of the Reactions

The nature of the reactions between the organometallic complex **1** and a wide variety of anilines has been established by the isolation and characterization of some of the anilinium adducts (4; X = H, 4-Me, 4-OMe, 4-Cl, or 2,6-(Me)₂) and by *in situ* IR and ¹H NMR spectral studies of several others [2, 3, 7, 19]. Their IR spectra showed two strong carbonyl bands at *c.* 2045 and 1970 cm⁻¹. The same two ν(CO) bands were observed during the IR studies of reactions (1) using a large excess of amine nucleophile, indicating the formation of the same tricarbonyl (1-4-η-5-exo-*N*-anilino-cyclohexa-1,3-diene) iron complexes. The reversibility of reactions (1) was demonstrated by the addition of a few drops of trifluoroacetic acid to equilibrium mixtures as obtained from the reactions; the original organometallic complex **1** was regenerated quantitatively, as evidenced by the appearance of strong ν(CO) bands at 2120 and 1965 cm⁻¹ and the disappearance of bands due to the products **4** at 2045 and 1970 cm⁻¹. The presence of the former bands in the reaction solutions of **1** even at infinite time further confirm that there is an equilibrium.

Kinetics and Mechanism

Kinetic results for the addition of anilines to complex **1** are listed in Table 1. Except for 4-methoxyaniline and 3,4-dimethylaniline which were studied under equimolar conditions, plots of *k*_{obs} versus [amine] are linear with non-zero intercepts, indicating the general two-term rate law (3).

$$\text{Rate} = k_a[\text{complex}][\text{amine}] + k_b[\text{complex}] \quad (3)$$

i.e. $k_{\text{obs}} = k_a[\text{amine}] + k_b$

The separate *k*_a and *k*_b values shown in Table 1 were calculated by a least-squares fit to eqn. (3). Rate law (3) may be rationalized in terms of an initial amine addition on **1** to form the cationic diene intermediate, [(1-4-η-diene·NH₂R)Fe(CO)₃] (**5**) from which the neutral products, [(1-4-η-diene·NHR)Fe(CO)₃] (**4**) are formed via amine-assisted proton removal [3]. Table 2 compares the results of the reactions of anilines with complexes **1**, **2** and **3** and demonstrates a decrease in rate along the sequence C₆H₇ > 2-MeOC₆H₆ > C₇H₉ (for example the relative rates for 4-methoxyaniline and 4-methylaniline are 1:3:30 and 1:3:17 respectively) indicating direct addition of the anilines to the dienyl rings of these complexes. Hammett plots for the reactions of anilines with all three dienyl complexes in CH₃CN at 0 °C are linear with slopes, ρ, of -3.23 for C₆H₇ (**1**) (Fig. 1), -2.70 for 2-MeOC₆H₆ (**2**) [14] and -2.06 for C₇H₉ (**3**) (Fig. 2). These results are summarized in Table 3 and the large negative slopes clearly suggest significant bond formation and a considerable build-up of positive charge on the nitrogen atom of the amine nucleophile in the transition states of these systems; the concentration of positive charge decreases along the sequence C₆H₇ > 2-MeOC₆H₆ > C₇H₉. Such transition states must be highly ordered (see refs. 7, 19 and 20) allowing some internal S_N2 process in the reformation of the starting dienyl complexes **1**, **2** or **3** (dissociative process) or protonation to the anilinium salt and the products **4** (associative process). Such a novel mechanism must be responsible for the large negative entropies of activation found [14, 19, 20] in the dissociative processes of amine additions to organometallics of the type **1**, **2** or **3**. The nature and magnitude of the slopes from the Hammett and Brønsted plots (Table 3) clearly support Odiaka's 'Ordered Transition State Mechanism' [7, 19, 20] and demonstrate that the extent to which the transition state is ordered depends on the electrophilicity of the organometallics being attacked by the amines. Thus the transition state becomes more ordered along the sequence C₇H₉ < 2-MeOC₆H₆ < C₆H₇ for amine additions to organometallics of the type **1**, **2** or **3** (Table 3) in accordance with their increasing electrophilicities.

Influence of Nucleophile Basicity

The results in Tables 1, 4 and 5 clearly reveal the dependence of rate on nucleophile basicity as pre-

TABLE 1. Kinetic results for reactions of $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7(\text{CO})_3)\text{BF}_4$ (1.5×10^{-3} mol dm $^{-3}$) with anilines in CH $_3$ CN at 0 °C

Nucleophile	θ C (°C)	$10^2 \times [\text{Nucleophile}]$ (mol dm $^{-3}$)	k_{obs} (s $^{-1}$)	k_{a}^{b} (dm 3 mol $^{-1}$ s $^{-1}$)	k_{b}^{b} (s $^{-1}$)
H $_2$ NC $_6$ H $_4$ MeO-4	0.0	0.15		17220(230) ^a	
H $_2$ NC $_6$ H $_3$ (Me) $_2$ -3,4	0.0	0.15		15890(140) ^a	
H $_2$ NC $_6$ H $_4$ Me-3	0.0	1.0	36.1		
	0.0	2.0	59.2		
	0.0	3.0	81.1		
	0.0	4.0	106.0		
	0.0	5.0	128.0		2306(19)
H $_2$ NC $_6$ H $_4$ MeO-3	0.0	1.0	30.5		
	0.0	2.0	48.1		
	0.0	4.0	78.6		
	0.0	5.0	93.5		
	0.0	6.0	111.0		1584(19)
H $_2$ NC $_6$ H $_4$ MeO-2	0.0	1.0	41.5		
	0.0	2.0	54.9		
	0.0	4.0	73.4		
	0.0	6.0	95.5		
	0.0	8.0	116.0		1050(18)
H $_2$ NC $_6$ H $_4$ Cl-3	0.0	1.0	18.4		
	0.0	2.0	19.8		
	0.0	4.0	21.4		
	0.0	6.0	23.9		
	0.0	8.0	26.1		108(3)
H $_2$ NC $_6$ H $_4$ Cl-2	0.0	2.5	27.0		
	0.0	5.0	27.3		
	0.0	10.0	27.5		
	0.0	15.0	27.8		
	0.0	20.0	28.2		6.39(0.38)

^aEstimated by a least-squares fit to eqn. (2) with standard errors of estimate in parentheses. ^bEstimated by a least-squares fit to eqn. (3) with standard errors of estimate in parentheses.

TABLE 2. Variation of rates with Hammett coefficients (σ) for the reactions of anilines with $[\text{Fe}(1\text{-}5\text{-}\eta\text{-dienyl})(\text{CO})_3]\text{BF}_4$ in CH $_3$ CN at 0 °C (dienyl = C $_6$ H $_7$, 2-MeOC $_6$ H $_6$ or C $_7$ H $_9$)

Amine	k_{a} (C $_6$ H $_7$) (dm 3 mol $^{-1}$ s $^{-1}$)	k_{a}^{a} (2-MeOC $_6$ H $_6$) (dm 3 mol $^{-1}$ s $^{-1}$)	k_{a}^{b} (C $_7$ H $_9$) (dm 3 mol $^{-1}$ s $^{-1}$)	σ^{c}
H $_2$ NC $_6$ H $_4$ MeO-4	17220	1730	578	-0.27
H $_2$ NC $_6$ H $_3$ (Me) $_2$ -3,4	15890		406	-0.24
H $_2$ NC $_6$ H $_4$ Me-4	6470	1010	386	-0.16
H $_2$ NC $_6$ H $_4$ Me-3	2306	373	199	-0.07
H $_2$ NC $_6$ H $_5$	2000	373	151	0.00
H $_2$ NC $_6$ H $_4$ Cl-4	657	82.1	48.4	+0.23
H $_2$ NC $_6$ H $_4$ Cl-3	108	33.6	27.7	+0.37

^aValues from ref. 3. ^bValues from ref. 20 except for H $_2$ NC $_6$ H $_4$ Cl-4 from ref. 19. ^cHammett coefficients from ref. 23.

viously established (see for example refs. 3 and 4). A Brønsted plot of $\log k$ against the $\text{p}K_{\text{a}}$ of the amine conjugate acid in H $_2$ O [24] (Fig. 3) gave a slope, α , of 1.14 ± 0.04 for addition of non-sterically crowded anilines to **1** indicating a very strong dependence of rate of amine basicity. This α value is

similar to those found for complexes **2** (0.94 ± 0.06) [3] and **3** (0.67 ± 0.20) [20]. However the decreasing values along the sequence C $_6$ H $_7$ > 2-MeOC $_6$ H $_6$ > C $_7$ H $_9$ (Table 3) is also consistent with the decreasing accumulation of positive charge on the N atom of the amine nucleophile in the respective transition

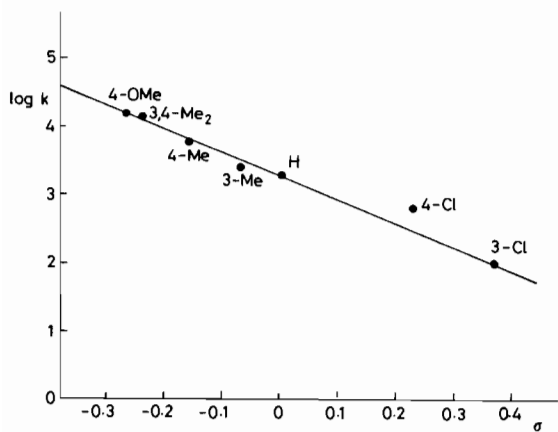


Fig. 1. Plot of $\log k$ vs. σ for the reactions of anilines with $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_6\text{H}_7)]\text{BF}_4$ in CH_3CN at 0°C ; slope = -3.23 ± 0.22 .

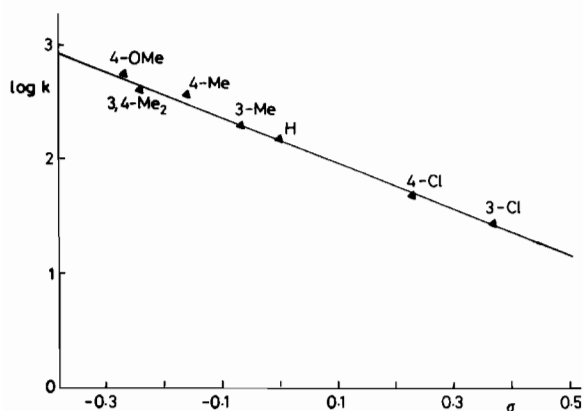


Fig. 2. Plot of $\log k$ vs. σ for the reactions of anilines with $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_7\text{H}_9)]\text{BF}_4$ in CH_3CN at 0°C ; slope = -2.06 ± 0.07 .

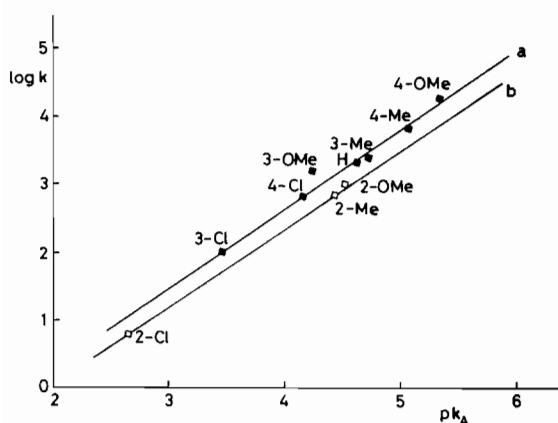


Fig. 3. Brønsted plots for the reactions of $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-C}_6\text{H}_7)]\text{BF}_4$ in CH_3CN at 0°C with (a) unhindered anilines, (b) anilines with 2-Cl or 2-Me or 2-OMe groups.

TABLE 3. Summary of slopes from Brønsted and Hammett plots for the reactions of anilines with $[\text{Fe}(1-5-\eta\text{-dienyl})(\text{CO})_3]\text{BF}_4$ in CH_3CN at 0°C

Dienyl	Slope, α (Brønsted)	Slope, ρ (Hammett)
C_6H_7	1.14 ± 0.04	-3.23 ± 0.22
2-MeOC ₆ H ₆	0.94 ± 0.06	-2.70 ± 0.12
C_7H_9	0.67 ± 0.20	-2.06 ± 0.07

TABLE 4. Variation of rates with amine basicity for the reactions of anilines with $[\text{Fe}(1-5-\eta\text{-C}_6\text{H}_7)(\text{CO})_3]\text{BF}_4$ in CH_3CN at 0°C

Amine	k_a ($\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$)	$\text{p}K_a^a$ (H_2O)
$\text{H}_2\text{NC}_6\text{H}_4\text{MeO-4}$	17220	5.34
$\text{H}_2\text{NC}_6\text{H}_4\text{Me-4}$	6470 ^b	5.08
$\text{H}_2\text{NC}_6\text{H}_4\text{Me-3}$	2306	4.73
$\text{H}_2\text{NC}_6\text{H}_5$	2000 ^b	4.63
$\text{H}_2\text{NC}_6\text{H}_4\text{MeO-3}$	1584	4.23
$\text{H}_2\text{NC}_6\text{H}_4\text{MeO-2}$	1050	4.52
$\text{H}_2\text{NC}_6\text{H}_4\text{Me-2}$	687 ^b	4.44
$\text{H}_2\text{NC}_6\text{H}_4\text{Cl-4}$	657 ^b	4.15
$\text{H}_2\text{NC}_6\text{H}_4\text{Cl-3}$	108	3.46
$\text{H}_2\text{NC}_6\text{H}_4\text{Cl-2}$	6.39	2.65

^a $\text{p}K_a$ values from ref. 4. ^bRate constants from refs. 14 and 19.

TABLE 5. Steric effects on rates for addition of anilines to $[\text{Fe}(1-5-\eta\text{-C}_6\text{H}_7)(\text{CO})_3]\text{BF}_4$ in CH_3CN at 0°C

Amine	k_a ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	k_a (relative)
$\text{H}_2\text{NC}_6\text{H}_5$	2000	5.6
$\text{H}_2\text{NC}_6\text{H}_4\text{Me-2}$	687	1.9
$\text{H}_2\text{NC}_6\text{H}_3(\text{Me})_2\text{-2,6}$	358 ^a	1.0

^aValue from ref. 7.

states in accordance with the decreasing electrophilicities of the organometallics. A similar observation has recently been made in the reactions of pyridines with complexes 1, 2 and 3 where α values decreased along the sequence C_6H_7 (0.97 ± 0.04) > 2-MeOC₆H₆ (0.43 ± 0.01) > C_7H_9 (0.39 ± 0.03) [25].

Steric Influence of Nucleophile

The steric effect of aniline additions to complex 1 is clearly demonstrated in Fig. 3 and Table 5 ($\text{H}_2\text{NC}_6\text{H}_5 > \text{H}_2\text{NC}_6\text{H}_4\text{Me-2} > \text{H}_2\text{NC}_6\text{H}_3(\text{Me})_2\text{-2,6}$; relative rates 5.6:1.9:1). The two straight lines shown in Fig. 3 are plots of $\log k$ against the $\text{p}K_a$ of the amine conjugate acid for (a) unhindered anilines and (b) anilines bearing a methyl, methoxy or chloride group at the 2-position. The distance of 0.3 log units between the two graphs indicates that there is a two-fold decrease in rate due to steric blocking at the 2-position of the aniline nucleophile. This is very

similar to the two-fold decrease in rate recently found [20] for aniline additions to complex 3. With the analogous pyridine reactions, a ten-fold decrease in rate has been found for all three organometallics 1, [4], 2 [25] and 3 [18] indicating the more pronounced steric influences in the pyridine additions than in the analogous aniline reactions. This observation is certainly not surprising since it is obvious that the N reaction centre in pyridines is considerably more sterically masked by *ortho*-substituents than is the N atom in the related anilines.

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