Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 19.† Addition of Anilines to Tricarbonyl(1—5-η-dienyl)iron Cations

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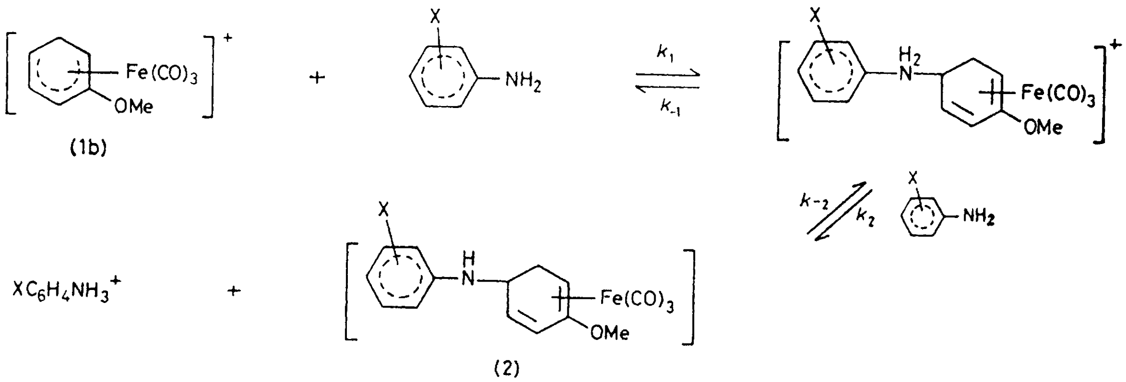
Spectroscopic and kinetic studies of the reactions below (X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-Cl, 4-OMe, or 4-NO_2) in CH_3CN have provided quantitative information on the importance of basicity and steric factors in controlling amine nucleophilicity towards co-ordinated π-hydrocarbons. Similar reactions with cations $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ (1a) and $[Fe(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3]^+$ (1c) have also been investigated. For the reactions of 4-methoxy- and 4-methyl-aniline with (1b), which proceed to completion, $k_{obs.} = k_1[\text{amine}]$. However, for the equilibrium



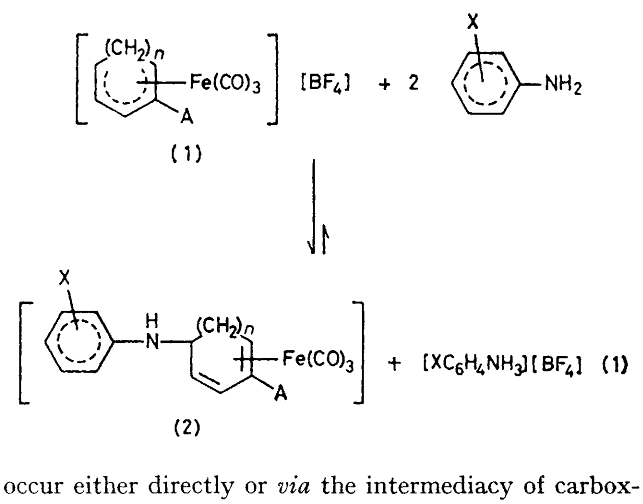
reactions of the other less basic amines with cations (1a)—(1c) the two-term expression $k_{obs.} = k_1[\text{amine}] + k_{-1}[H^+]/([H^+] + K_2K_a)$ is indicated. The general rate trend C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9 and the low $\Delta H^‡_1$ and large negative $\Delta S^‡_1$ values are consistent with direct addition to the dienyl rings. For attack by non-sterically crowded anilines on (1b), a Brönsted plot of log k_1 *versus* pK_a of the amine conjugate acid (in H_2O) has a high slope of 1.0, indicating a very strong dependence of k_1 on amine basicity. A Hammett plot for this reaction gives a slope of −2.7, indicating significant bond formation and build-up of positive charge on the aniline nitrogen atom in the transition state. The steric retardation of k_1 caused by blocking substituents in the 2-position of the anilines is considerably smaller than that previously found for the related additions of pyridines to cations (1a)—(1c).

Nucleophilic addition to the dienyl ring of $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ (1a) by aniline and 4-methylaniline has been recently reported,[1-3] giving neutral substituted-diene products of the type (1—4-η-5-*exo*-*N*-anilinocyclohexa-1,3-diene)tricarbonyliron in high yield. Similar reactions have also been described[4-6] with the related acyclic dienyl cations. These processes contrast with the behaviour of the analogous cyclopentadienyl complex $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ towards amines, where nucleophilic attack occurs instead on a carbonyl ligand to give carboxamido-products.[7]

At present little quantitative information is available concerning the factors controlling nucleophilicity towards co-ordinated π-hydrocarbons. Substituted anilines provide a particularly convenient series for investigating the influence of electronic and steric effects on nucleophile reactivity. A detailed synthetic and mechanistic study has therefore been undertaken of the reactions of a wide range of anilines $XC_6H_4NH_2$ (X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-Cl, 4-OMe, 3-NO_2) with the complexes (1a), $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3][BF_4]$ (1b), and $[Fe(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3][BF_4]$(1c) in acetonitrile [equation (1) (n = 1 or 2; A = H or OMe)].

† Part 18, D. J. Evans, L. A. P. Kane-Maguire, and D. A. Sweigart, *J. Organomet. Chem.*, 1981, **215**, C27.

Apart from providing rare quantitative information on the importance of factors such as amine basicity, reactions (1) pose several interesting mechanistic problems. For example, addition to the dienyl rings may



occur either directly or *via* the intermediacy of carboxamido-species. Furthermore, since two amine molecules are consumed in the processes, they could occur in either a concerted or step-wise fashion. The reactions with 4-

methylaniline have been described elsewhere,[3] and a preliminary report has appeared.[8]

EXPERIMENTAL

Materials.—The complexes (1a), (1b), and (1c) were prepared and purified using published procedures.[9,10] Aniline and substituted anilines were purchased in the purest grades available (BDH or Aldrich). The liquids were freshly distilled under a dinitrogen atmosphere and dried over molecular sieves (grade 3A) prior to use. The solids were used as supplied. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves under a dinitrogen atmosphere.

The neutral substituted-diene products (2) from the reactions of aniline with (1a), and of 4-methylaniline with cations (1a), (1b), and (1c) have been isolated and fully characterised elsewhere.[1-3] The related products (2) from the reactions of other substituted anilines in equation (1) have been characterised here from *in situ* ^1H n.m.r. and i.r. spectroscopic studies (see below). For the *in situ* ^1H n.m.r. experiments in $[^2H_3]$acetonitrile or $[^2H_6]$acetone the dienyl-iron salt concentrations were generally 0.25 mol dm^{-3} and [amine] = 0.50 mol dm^{-3}. However, in the cases of 3-chloro- and 2-methyl-aniline a ten-fold excess of amine was employed, *i.e.* [amine] = 2.5 mol dm^{-3}, in order to drive these less favourable reactions to completion.

Tricarbonyl[1—4-η-5-(N-4-*methoxyanilino*)*cyclohexa*-1,3-*diene*]*iron*, (2a).—Hydrogen-1 n.m.r.: (CD_3CN) τ 3.0—3.3 (4 H, overlaps with anilinium peak, aromatic), 4.45 (2 H, overlapping resonances, H^2 and H^3), 5.6 (1 H, br, –NH), 6.32 (3 H, s, $-OCH_3$), 7.0 (2 H, overlapping resonances, H^1 and H^4), 7.70 (1 H, m, $H^{6'}$), 8.50 (1 H, m, H^6); (CD_3COCD_3) τ 2.7—3.3 (4 H, overlaps with anilinium peak, aromatic), 4.40 (2 H, overlapping resonances, H^2 and H^3), 5.6 (1 H, br, –NH), 5.90 (1 H, m, $H^{5'}$), 6.32 (3 H, s, $-OCH_3$), 6.85 (2 H, overlapping resonances, H^1 and H^4), 7.70 (1 H, m, $H^{6'}$), 8.50 (1 H, m, H^6).

Tricarbonyl[1—4-η-5-(N-3-*methylanilino*)*cyclohexa*-1,3-*diene*]*iron*, (2b).—Hydrogen-1 n.m.r. (CD_3CN): τ 2.75—3.45 (4 H, overlaps with anilinium peaks, aromatic), 4.45 (2 H, overlapping resonances, H^2 and H^3), 5.6 (1 H, br, –NH), 6.20 (1 H, m, $H^{5'}$), 6.90 (2 H, overlapping resonances, H^1 and H^4), 7.5—7.95 (4 H, overlaps with anilinium peaks, $H^{6'}$ and $-CH_3$), 8.50 (1 H, m, H^6).

Tricarbonyl[1—4-η-5-(N-3-*chloroanilino*)*cyclohexa*-1,3-*diene*]*iron*, (2c).—Hydrogen-1 n.m.r. (CD_3CN): τ 2.8—3.5 (overlaps with anilinium peaks, aromatic), 4.5 (2 H, overlapping resonances, H^2 and H^3), 5.4 (1 H, br, –NH), 6.1 (1 H, m, $H^{5'}$), 6.85 (2 H, overlapping resonances, H^1 and H^4), 7.7 (4 H, m, $H^{6'}$), 8.6 (1 H, m, H^6).

Tricarbonyl[1—4-η-5-(N-4-*methoxyanilino*)*cyclohepta*-1,3-*diene*]*iron*, (2d).—Hydrogen-1 n.m.r. (CD_3COCD_3): τ 2.5—3.3 (4 H, overlaps with anilinium peak, aromatic), 4.5 (2 H, overlapping resonances, H^2 and H^3), 5.9 (1 H, m, $H^{5'}$), 6.32 (3 H, s, $-OCH_3$), 6.9 (2 H, overlapping resonances, H^1 and H^4), 7.5—8.0 (masked by acetone, $H^{6'}$ and $H^{7'}$), 8.2—8.95 (2 H, overlapping resonances, H^6 and H^7).

Tricarbonyl[1—4-η-5-(N-2-*methylanilino*)*cyclohepta*-1,3-*diene*]*iron*, (2e).—Hydrogen-1 n.m.r. (CD_3COCD_3): τ 3.0—3.4 (4 H, overlaps with anilinium peaks, aromatic), 4.7 (2 H, overlapping resonances, H^2 and H^3), 6.3 (1 H, m, $H^{5'}$), 6.95 (2 H, overlapping resonances, H^1 and H^4), 7.4—7.8 (masked by acetone, $H^{6'}$ and $H^{7'}$), 7.98 (3 H, s, $-CH_3$), 8.3 (2 H, overlapping resonances, H^6 and H^7).

Spectroscopic Studies.—Hydrogen-1 n.m.r. spectra (90 MHz) were recorded on a Perkin-Elmer R32 spectrophotometer using either $[^2H_3]$acetonitrile or $[^2H_6]$acetone as solvent. Infrared spectra were measured on a Perkin-Elmer 257 spectrophotometer using matched 0.5-mm sodium chloride solution cells.

Equilibrium Studies.—Equilibrium constants for the overall processes (1) (n = 1 or 2; A = H or OMe; X = H, 2-Me, or 4-Cl) were determined by dissolving the appropriate

TABLE 1

Overall equilibrium constants ($K_{eq.} = K_1K_2$) for the reactions of anilines with $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ cations in CH_3CN at 20 °C *

Dienyl	Amine	$K_{eq.}/dm^3\ mol^{-1}$	Ref.
C_6H_7	4-Methylaniline	940	3
	Aniline	42 (47)	This work
	2-Methylaniline	6	This work
	4-Chloroaniline	1.4	This work
$2\text{-}MeOC_6H_6$	4-Methylaniline	27	3
	Aniline	2.3 (2.1)	This work
	2-Methylaniline	0.6	This work
C_7H_9	4-Methylaniline	540	3
	2-Methylaniline	1.1 (1.2)	This work

* Values in parentheses at 0 °C.

dienyl salts in acetonitrile solutions (20 °C) of the amines of varying concentrations, and recording the i.r. spectra in the region 1 900—2 200 cm^{-1}. The equilibrium concentrations of the unreacted $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ ions were calculated from their absorption at 2 120 cm^{-1}, using their known[11] absorption coefficients. From the known starting concentrations, the equilibrium concentrations of the products (2) could then be estimated, allowing calculation of the equilibrium constants $K_{eq.}$ using equation (2).

$$K_{eq.} = \frac{[Fe\{1—4\text{-}\eta\text{-}5\text{-}(NHC_6H_4X)diene\}(CO)_3][XC_6H_4NH_3^+]}{[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3^+][XC_6H_4NH_2]^2} \quad (2)$$

Kinetic Studies.—Each of the reactions (1) were rapid, and were studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer. Separate solutions of the complex salts (1.5×10^{-3} mol dm^{-3}) and amine (0.01—0.40 mol dm^{-3}) were freshly prepared and thermostatted at the desired temperature prior to mixing.

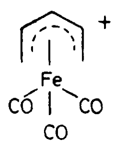
The reactions were monitored at 390 nm, at which wavelength a large decrease in absorbance was observed. Reaction traces were stored on a Tektronix 564B storage oscilloscope fitted with a log converter, giving direct absorbance read-out. All reactions were carried out using a large excess of nucleophile, and pseudo-first-order rate constants $k_{obs.}$ were calculated from the gradients of plots of $\log(A_t - A_\infty)$ *vs.* time. Linear first-order kinetics were generally obtained for at least two half-lives. Each run was repeated at least three times to provide average $k_{obs.}$ values (reproducibility ±3%).

Activation enthalpies were obtained from a least-squares fit to the Arrhenius equation. The errors quoted are the standard deviations derived from the least-squares analyses. Entropies of activation were estimated using the second-order rate constants, k_1 (see below).

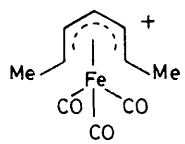
RESULTS AND DISCUSSION

Spectroscopic Studies.—The nature of the products (2) obtained from the reactions of 4-methoxy- and 2-methylaniline with cations (1a) and (1c), and of 3-chloroaniline with (1a), are clearly established from their *in situ* ^{1}H n.m.r. spectra (see Experimental section). Under the conditions employed for these ^{1}H n.m.r. studies each of the reactions proceeds to completion. The spectra of the products are fully consistent with neutral tricarbonyl-(substituted-1,3-diene)iron species, and are very similar to those previously reported for analogous products with aniline [1,2] and 4-methylaniline.[3] These *in situ* ^{1}H n.m.r. studies also confirm the formation of the appropriate anilinium salts $[XC_6H_4NH_3][BF_4]$.

The amine substituents in products (2) are assumed to be in an *exo*-position by analogy with the established [2] structure of the anilino-product (1—4-η-5-*N*-anilino-cyclohexa-1,3-diene)tricarbonyliron. *exo*-Addition of the various anilines to cations (1a)—(1c) is also strongly supported by kinetic studies (see below). Additional support comes from a comparison with previous studies [4-6] of the reactions of various anilines with [Fe(acyclic dienyl)(CO)$_3$]$^+$ cations. Maglio and Palumbo [4] have found that addition to cation (3) leads not only to the expected products [Fe(diene–NHR)(CO)$_3$] (4), but also to the binuclear species [(CO)$_3$Fe(diene–NR–diene)Fe-(CO)$_3$] (5), arising from nucleophilic attack by the initial product (4) on (3). However, the more sterically demanding cation (6) gave only '(4)-type' products.[5]



(3)



(6)

Similarly, our failure to observe any binuclear products related to species (5) from reactions (1) may be explained in terms of steric hindrance by the methylene group(s) of the dienyl rings in cations (1a)—(1c) preventing approach by the potentially nucleophilic products (2).

In all of the processes (1) studied here the i.r. spectra of the reaction solutions in CH_3CN are also consistent with the formation of tricarbonyl(substituted diene)iron species, with two product ν(CO) bands appearing at *ca.* 2 045 and 1 970 cm^{-1}. Under the kinetic conditions employed ([Fe] = 1.5×10^{-3} mol dm^{-3}, [amine] $\geqslant 1.0 \times 10^{-2}$ mol dm^{-3}), the reaction of 4-methoxyaniline with cation (1b) proceeds to completion. However, all the other reactions with less basic anilines are equilibrium processes, since reaction solutions at infinite time also exhibit ν(CO)

TABLE 2

Kinetic results for addition of 4-methoxyaniline to [Fe(1—5-η-2-MeOC$_6$H$_6$)(CO)$_3$][BF$_4$] in CH_3CN at 0.0 °C [a]

10^2[amine]/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1/dm^3 mol^{-1} s^{-1}
1.0	17.2	
1.5	25.9	1 730(21) [b]
2.0	35.1	
2.8	48.2	

[a] [Fe] = 1.5×10^{-3} mol dm^{-3}. [b] Calculated from a least-squares fit to equation (3).

bands at 2 120 and 1 965 cm^{-1} due to the original dienyl salts. Equilibrium constants ($K_{eq.}$) calculated for the overall reactions (1) are collected in Table 1, together with previous values for 4-methylaniline.[3]

Although no carbonyl bands other than those assignable to the dienyl cations (1) and products (2) were observed during any of the present kinetic studies, equimolar mixtures of aniline and (1a) ([Fe] = [$C_6H_5NH_2$] = 1.5×10^{-3}—6.0×10^{-3} mol dm^{-3}) show an additional

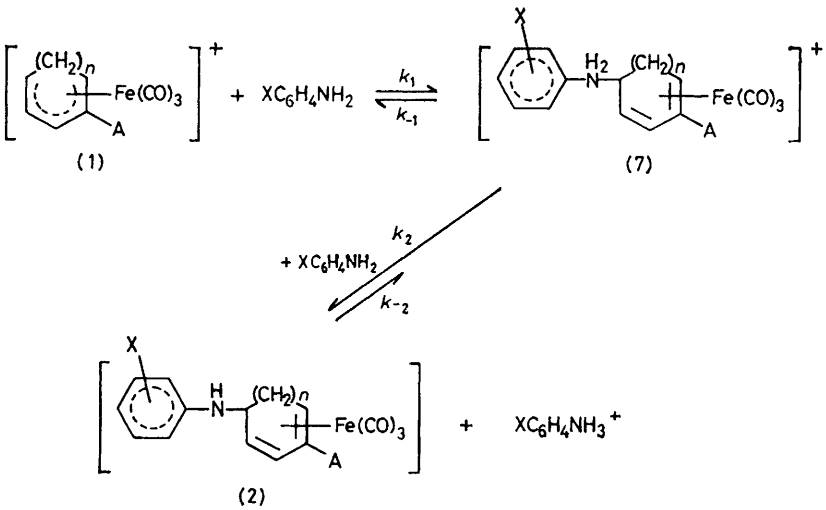
TABLE 3

Kinetic results for addition of aniline to [Fe(1—5-η-dienyl)(CO)$_3$][BF$_4$] complexes in CH_3CN *

Dienyl	Temp./°C	10^2 [amine]/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_a/dm^3 mol^{-1} s^{-1}	k_b/s^{-1}
C_6H_7	0.0	2.0	59.9		
	0.0	3.0	85.2		
	0.0	4.0	100	2 000(56)	21.6(2.2)
	5.0	1.0	50.6		
	5.0	2.0	74.1		
	5.0	3.0	94.2	2 180(18)	29.3(1.0)
	15.1	1.0	69.1		
	15.1	1.5	81.2		
	15.1	2.0	94.4	2 560(11)	43.4(0.2)
2-MeOC$_6$H$_6$	0.0	1.0	7.68		
	0.0	2.0	11.4		
	0.0	4.0	18.3		
	0.0	5.0	22.1		
	0.0	8.0	33.8		
	0.0	10.0	41.2	373(3)	3.7(0.2)
	5.1	2.0	13.4		
	5.1	4.0	21.0		
	5.1	5.0	25.6		
	5.1	8.0	37.7		
	5.1	10.0	45.6	405(3)	5.2(0.2)
	10.4	2.0	19.7		
	10.4	4.0	29.6		
	10.4	8.0	49.1		
	10.4	10.0	58.8	488(1)	10.0(0.1)
	13.0	1.1	18.8		
	13.0	2.2	25.4		
	13.0	5.2	41.1	540(9)	13.1(0.3)
	15.1	2.0	27.1		
	15.1	4.0	40.1		
	15.1	5.0	46.7		
	15.1	10.0	75.0	594(11)	16.0(0.7)
	20.0	4.0	49.2		
	20.0	5.0	54.2		
	20.0	10.0	87.1	641(13)	23.0(0.9)

* [Fe] = 1.5×10^{-3} mol dm^{-3}.

weak shoulder at *ca.* 1 990 cm^{-1}. By analogy with the previously studied [3] 4-methylaniline reaction, this band is assigned to the intermediate cationic species [Fe(C_6H_7·$NH_2C_6H_5$)(CO)$_3$]$^+$ (7), its expected second carbonyl peak being masked by the original dienyl cation band at 2 065 cm^{-1}. This observation supports the general step-wise mechanism shown in the Scheme for reactions (1). Assuming this mechanism, the calculated $K_{eq.}$ values may be equated with K_1K_2. In addition, the presence of only very small amounts of the intermediate species (7) in equilibrium mixtures indicates that K_2, the equilibrium constant for amine-assisted proton removal, is large. This in turn suggests that the relative magnitudes of the overall $K_{eq.}$ values for each amine in reactions (1) are largely determined by the relative sizes of K_1. The marked decrease in $K_{eq.}$ along the series 4-methylaniline



SCHEME

> aniline > 2-methylaniline > 4-chloroaniline demonstrates the importance of amine basicity.

Finally, it is noteworthy that each of the reactions (1) may be reversed quantitatively and rapidly by the addition of excess trifluoroacetic acid.

Kinetics and Mechanism.—Kinetic results for reactions (1) at various temperatures and amine concentrations are summarised in Tables 2—5.

Reaction with 4-*methoxyaniline*. For the addition of 4-methoxyaniline to cation (1b), $k_{obs.}$ obeys the simple equation (3). Similar behaviour has been previously

$$k_{obs.} = k[RNH_2] \quad (3)$$

reported[3] for the related reactions of 4-methylaniline with cations (1a)—(1c). The absence of a second-order dependence of $k_{obs.}$ on [amine] eliminates a concerted process involving base-catalysed nucleophilic attack by amine, as has been proposed for carboxamido-formation[12] with *trans*-$[M(CO)_4(PR_3)_2]^+$ (M = Mn or Re) and for the reactions of amines with pentacarbonyl(methoxycarbene)chromium to give the corresponding aminocarbene complexes.[13]

Expression (3) may be rationalised in terms of the mechanism outlined in the Scheme. Assuming a steady-state concentration for the intermediate (7) (and assuming k_{-2} is negligible since the reactions proceed to completion under the kinetic conditions), this Scheme leads to the general rate expression (4). Provided $k_2[RNH_2] \gg k_{-1}$, this equation simplifies to the observed form (3),

$$k_{obs.} = k_1k_2[RNH_2]^2/(k_{-1} + k_2[RNH_2]) \quad (4)$$

in which the calculated second-order rate constants k refer to the initial ring-addition step, k_1. Rapid proton removal (k_2) from intermediate (7) is not unreasonable since the $Fe(diene)(CO)_3$ moiety is known[14] to be an electron-withdrawing group.

An alternative explanation for the observed rate law (3) may also be sought in terms of a pre-equilibrium mechanism, *i.e.* assuming k_1 and k_{-1} in the Scheme are very much faster than k_2. This mechanism predicts the

TABLE 4

Kinetic results for addition of 2-methylaniline to Fe[(1—5-η-dienyl)(CO)$_3$][BF$_4$] complexes in CH$_3$CN *

Dienyl	Temp./°C	10^2 [amine]/mol dm^{-3}	$k_{obs.}$/s^{-1}	k_a/dm^3 mol^{-1} s^{-1}	k_b/s^{-1}
C_6H_7	0.0	1.0	19.0		
	0.0	2.0	25.8		
	0.0	4.0	39.6		
	0.0	5.0	46.4	687(1)	12.1(0.1)
	10.1	1.0	34.2		
	10.1	2.0	46.4		
	10.1	5.0	85.0	1 270(8)	21.2(0.2)
	15.3	1.0	48.0		
	15.3	2.0	64.6		
	15.3	5.0	114	1 650(2)	31.5(0.1)
2-MeOC$_6$H$_6$	0.0	1.0	6.64		
	0.0	2.0	7.33		
	0.0	3.0	7.79		
	0.0	4.0	8.25		
	0.0	5.0	9.11		
	0.0	10.0	11.7	55.9(2)	6.1(0.1)
	9.9	1.0	12.1		
	9.9	2.0	13.6		
	9.9	4.0	15.8		
	9.9	5.0	17.4		
	9.9	10.0	23.7	128(2)	10.9(0.1)
	15.3	1.0	17.1		
	15.3	2.0	18.9		
	15.3	4.0	22.1		
	15.3	5.0	24.5		
	15.3	10.0	33.2	179(3)	15.3(0.2)
	20.2	4.0	32.5		
	20.2	5.0	35.0		
	20.2	10.0	46.5	233(2)	23.3(0.1)
C_7H_9	0.0	5.0	2.81		
	0.0	10.0	5.48		
	0.0	20.0	9.88		
	0.0	30.0	13.9		
	0.0	40.0	18.0	43.0(1)	1.00(0.2)
	10.0	5.0	5.26		
	10.0	10.0	8.67		
	10.0	20.0	15.9	71.0(1)	1.65(0.1)
	20.3	5.0	8.98		
	20.3	10.0	14.4		
	20.3	20.0	26.1	114(1)	3.15(0.2)

* [Fe] = 1.5×10^{-3} mol dm^{-3}.

TABLE 5

Kinetic results for addition of other anilines to [Fe(1—5-η-2-$MeOC_6H_6$)$(CO)_3$][BF_4] in CH_3CN at 0.0 °C *

Amine	10^2 [amine]/mol dm^{-3}	$k_{obs.}/s^{-1}$	k_a/dm^3 mol^{-1} s^{-1}	k_b/s^{-1}
3-Methylaniline	1.0	9.76		
	2.0	13.1		
	3.0	17.6		
	4.0	20.9	373(3)	6.0(0.2)
	5.0	24.7		
	10.0	43.2		
4-Chloroaniline	1.25	6.42		
	2.50	7.64	82(1)	5.5(0.1)
	10.0	13.7		
3-Chloroaniline	2.0	5.66		
	5.0	6.40	33.6(0.7)	4.9(0.1)
	10.0	8.22		
	20.0	11.6		
2-Chloroaniline	4.0	11.0		
	5.0	11.0		
	10.0	11.1	2.0(0.2)	10.9(0.1)
	20.0	11.3		
	40.0	11.7		

* [Fe] = 1.5×10^{-3} mol dm^{-3}.

general expression (5), which simplifies to (6) if $K_1[RNH_2]$

$$k_{obs.} = k_2K_1[RNH_2]^2/(1 + K_1[RNH_2]) \quad (5)$$

$$k_{obs.} = k_2[RNH_2] \quad (6)$$

$\gg 1$. However, this condition is clearly not met since no i.r. spectroscopic evidence was found for an intermediate under any of the kinetic conditions employed.

Reactions with less basic amines. In contrast to the above behaviour with 4-methoxy- and 4-methyl-aniline, plots of $k_{obs.}$ *versus* $[RNH_2]$ for each of the other amines studied are linear with a non-zero intercept (*e.g.*, see Figure 1), indicating the general two-term expression (7). The separate k_a and k_b values shown in

$$k_{obs.} = k_a[RNH_2] + k_b \quad (7)$$

Tables 3—5 were derived from a least-squares fit to equation (7).

This two-term form (7) found for $k_{obs.}$ may also be interpreted *via* the Scheme. Since the reactions with the less basic amines involve two successive equilibria, derivation of a general rate expression would be complex. However, by making the reasonable assumption that the establishing of equilibrium K_2 occurs much more rapidly than K_1, one obtains the relationships (8) and (9).

$$k_a = k_1 \quad (8)$$

$$k_b = k_{-1}[H^+]/([H^+] + K_2K_a) \quad (9)$$

Strong support for this view that k_a represents k_1, the second-order rate constant for direct nucleophilic addition at the dienyl rings, comes from the trend in k_a values down the series C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9 (18 : 2 : 1) found for the reactions of 2-methylaniline with cations (1a)—(1c) at 10 °C (Table 4). A similar variation in k_a with π-hydrocarbon is observed for the aniline reactions (Table 3). This trend is also the same as that previously observed for the reactions of cations (1a)—(1c) with

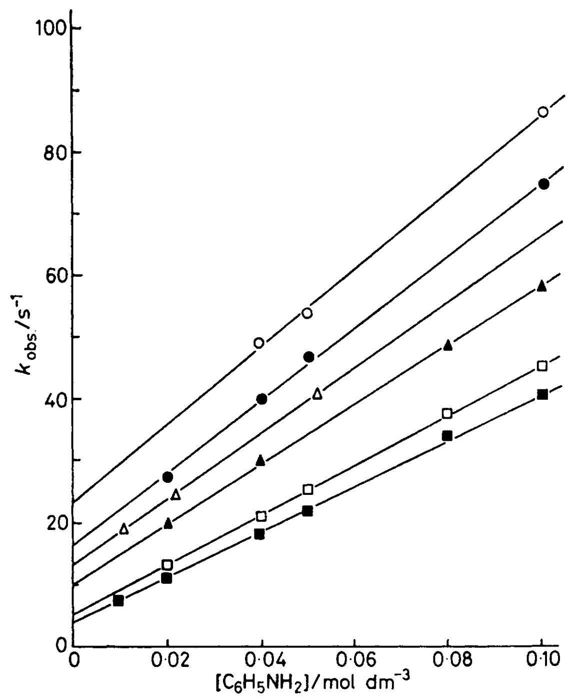


FIGURE 1 Dependence of $k_{obs.}$ on $[RNH_2]$ for the reaction of [Fe(1-5-η-2-$MeOC_6H_6$)$(CO)_3$][BF_4] with aniline at various temperatures (°C) in CH_3CN: 0.0 (■), 5.1 (□), 10.4 (▲), 13.0 (△), 15.1 (●), 20.0 °C (○)

phosphines [15] and pyridines,[16] processes known to involve direct addition to the dienyl rings. The slower rate for the 2-$MeOC_6H_6$ complex compared with the parent cyclohexadienyl complex is in accordance with the mesomeric and slight steric influence of the methoxide group, while the cycloheptadienyl cation (1c) is expected to show the slowest rate on steric grounds for reactions involving addition of a nucleophile from above the dienyl rings. The above rate trend also supports the assignment of an *exo*-configuration to the anilino-substituents in products (2) (see above).

The low enthalpies of activation and the large negative entropies of activation obtained for k_a in the reactions of aniline and 2-methylaniline with cations (1a)—(1c) are also consistent with simple addition (k_1) to the dienyl rings (Table 6). With aniline, the greater reactivity of the C_6H_7 complex compared with that of 2-$MeOC_6H_6$ is seen to arise from a much lower $\Delta H_a^‡$, suggesting enthalpy control over the relative rates. However, with 2-methylaniline a play-off between enthalpy and entropy effects can be seen. The rapidity of the reaction of the C_6H_7 complex compared with that of C_7H_9 arises from a markedly less negative $\Delta S_a^‡$ value (despite a slightly higher $\Delta H_a^‡$), while the intermediate rate for the 2-$MeOC_6H_6$ complex is associated with the least negative $\Delta S_a^‡$ and the highest $\Delta H_a^‡$ value.

Comparison of the activation parameters for the two sterically non-congested amines in Table 6 indicates that the trend in k_a, namely 4-methylaniline [3] > aniline, is entropy controlled. With both cations (1a) and (1b) the

TABLE 6

Rate and activation parameters for the reactions of anilines with $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3][BF_4]$ complexes in CH_3CN

Dienyl	Amine *	k_a (0 °C)/ dm^3 mol^{-1} s^{-1}	$\Delta H_a^‡$/kJ mol^{-1}	$\Delta S_a^‡$/J K^{-1} mol^{-1}
C_6H_7	4-Methylaniline	6 470	24.4(0.3)	−82(2)
	Aniline	2 000	8.2(0.2)	−150(4)
	2-Methylaniline	687	35.3(0.7)	−60(3)
2-$MeOC_6H_6$	4-Methylaniline	1 010	42.3(1.3)	−32(5)
	Aniline	373	17.1(1.1)	−132(4)
	2-Methylaniline	55.9	45.1(1.9)	−45(7)
C_7H_9	4-Methylaniline	386	27.9(1.0)	−93(4)
	2-Methylaniline	43	29.7(0.1)	−104(2)

* Data for 4-methylaniline are from ref. 3.

slower rates for aniline arise from the very negative $\Delta S_a^‡$ values, despite the significantly lower enthalpies of activation compared with 4-methylaniline.

In view of the relationship (9), quantitative interpretation of the k_b values in Tables 3—5 is difficult. Values of K_a are unavailable for the various amines in CH_3CN solvent, and $[H^+]$ has not been measured during these reactions because of experimental difficulties in non-aqueous solvents. Interestingly, if $[H^+] \gg K_2K_a$, then equation (9) collapses to the simple relationship (10). However, $\Delta S_b^‡$ values calculated assuming equation (10)

$$k_b = k_{-1} \qquad (10)$$

are generally negative, suggesting that this latter condition is not fulfilled.

Influence of Nucleophile Basicity.—The k_a (or k_1) values summarised in Table 7 for anilines without substituents in the 2-position (which will give rise to complicating steric effects) reveal a very marked dependence on the basicity of the amine nucleophile. Also consistent with this is the absence of any apparent reaction between (1a) and the very weakly basic 3-nitroaniline (although this may arise from a very unfavourable equilibrium constant, K_1K_2). This strong dependence of k_1 on amine basicity is demonstrated quantitatively for cation (1b) by the linear free-energy relationship obtained on plotting log k_1 *vs.* pK_a of the amine conjugate acid (in H_2O) [17] (Figure 2). Reactions

TABLE 7

Variation of k_1 with amine basicity for reactions of anilines $(XC_6H_4NH_2)$ with $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3][BF_4]$ in CH_3CN at 0 °C

X	k_1/dm^3 mol^{-1} s^{-1}	pK_a (H_2O)
4-OMe	1 730	5.34
4-Me	1 010 *	5.08
3-Me	373	4.73
H	373	4.63
4-Cl	82.1	4.15
3-Cl	33.6	3.46

* From ref. 3.

(1) with cation (1b) thus obey the Brönsted relationship (11), with a slope (α) of 1.0.

$$\log k_1 = \alpha \, pK_a + \text{constant} \qquad (11)$$

Interestingly, a slope of 1.0 has also been recently obtained [16] for the related additions of pyridines to cation (1a). These high slopes contrast with the very low α values of *ca.* 0.05 reported for attack by pyridines (py) and other amines on the very ' soft ' Pt^{II} centre in complexes such as *trans*-$[Pt(py)_2Cl_2]$.[18] Amine attack on moderately ' soft ' substrates such as alkyl halides has been reported [19] to give α values of *ca.* 0.4. Higher α

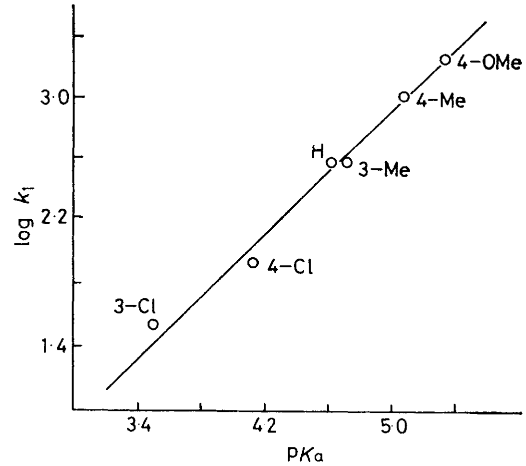


FIGURE 2 Plot of log k_1 *versus* pK_a for the reaction of anilines $(XC_6H_4NH_2)$ with $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3][BF_4]$ in CH_3CN at 0 °C; slope = 1.0

values of *ca.* 0.5 have been found for amine addition to free carbonium ions.[20] Following the reasoning of Pearson *et. al.*,[21] the present results therefore suggest that the dienyl rings in cations (1a)—(1c) are ' hard ' moieties. This view is in agreement with the relatively high positive charge calculated [22,23] to reside on the ring carbons of such cations.

Comprehensive pK_a values for anilines are not yet available in CH_3CN. However, studies by Streuli [24] and Hall [25] indicate that the base strengths of various amines in organic solvents such CH_3CN and CH_3NO_2 parallel those in water. For instance, the relationship pK_a = 11.69 − 0.0124 (Δh.n.p.) was observed [25] between the pK_a values in water and the half-neutralization points in CH_3NO_2.

In addition, an excellent straight line is also obtained on plotting log k_1 *versus* σ (the Hammett coefficient for the various X substituents) for reactions (1) with cation (1b) (Figure 3). This Hammett plot has a large negative slope of −2.7, indicating significant bond formation and considerable build-up of positive charge on the aniline nitrogen atom in the transition state. This large negative slope is very similar to that reported [26] for the reaction of anilines with benzoyl chloride.

Steric Effects of the Nucleophile.—The results in Tables 2—5 reveal, as expected, a marked decrease in k_1 upon introducing sterically blocking methyl- or chloro-substituents in the 2-position of the aniline nucleophile. For example, for addition to cation (1b), k_1 decreases in the order aniline > 2-methylaniline > 2-chloroaniline (180 : 28 : 1). These effects, however, are complicated by concomitant basicity variations caused by the substituents.

Nevertheless, a quantitative estimation of the steric influence of a 2-methyl (or 2-chloro-) group can be obtained from the separation Δ of 2-methyl- (or 2-chloro-) aniline below the Brönsted plot shown in Figure

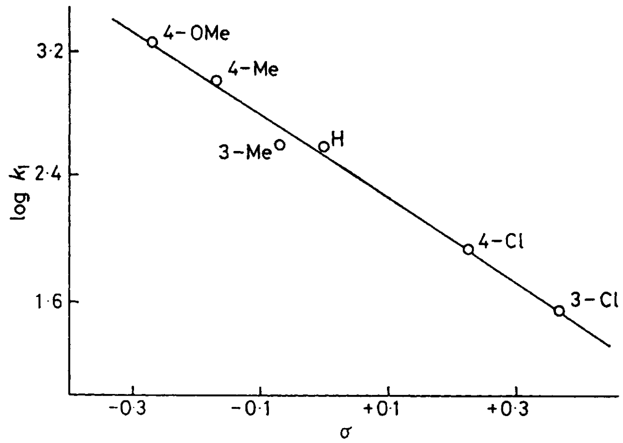


FIGURE 3 Plot of log k_1 *versus* σ for the reaction of anilines ($XC_6H_4NH_2$) with [Fe(1—5-η-2-MeOC$_6$H$_6$)(CO)$_3$][BF$_4$] in CH_3CN at 0 °C; slope = 2.7

2. For 2-methylaniline, the Δ value of *ca.* 0.4 indicates a 2—3 fold decrease in k_1 relative to the non-sterically crowded anilines. This compares with the Δ value of *ca.* 1.0 (*i.e.*, a 10-fold rate decrease) caused by a 2-methyl group in the related additions of pyridines to cation (1a).[16] This difference is not surprising, since the N reaction centre in pyridines is considerably more sterically masked by *ortho*-substituents than is the N atom in anilines.

In conclusion, it is now quantitatively established that for addition of anilines and pyridines [16] to co-ordinated π-hydrocarbons in complexes of type (1) the basicity of the amine nucleophile is a major factor in determining nucleophilicity. The relative importance of other nucleophile properties such as polarisability is currently being investigated.

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