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Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES.

XIV*. THE SIGNIFICANCE OF AMINE BASICITY IN DETERMINING THE NUCLEOPHILICITIES OF PYRIDINES AND ANILINES TOWARDS $[(1\text{-}5\text{-}\eta\text{-Dienyl})Fe(CO)_3]^+$ CATIONS

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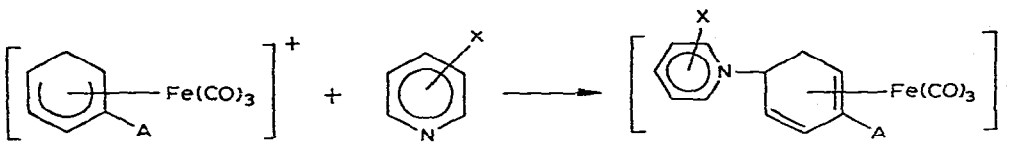
Summary

The second-order rate constants, k_1, for addition of pyridines and anilines to the cations $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ (I), $[(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3]^+$ (II), and $[(1\text{-}5\text{-}\eta\text{-}C_7H_9)Fe(CO)_3]^+$ (III) in CH_3CN decrease along the series I > II > III. The Brönsted relationship, $\log k_1 = \alpha pK_a$ + constant, is obeyed for the addition of substituted pyridines to I and of substituted anilines to II. The slopes, α, of about 1.0 in each case indicate a strong dependence of k_1 on amine basicity. These results, together with previous data on related phosphine additions, suggest a "hard" character for the dienyl ligands in these organometallic cations.

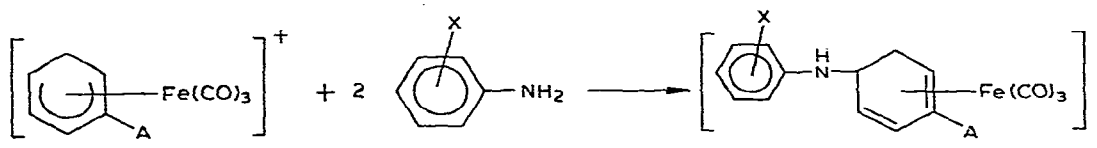
Although the reactions of nucleophiles with $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ complexes are of considerable synthetic interest, the factors governing the reactivity of such coordinated π-hydrocarbons are as yet poorly understood. Some progress has been made recently in establishing the relative reactivity of a variety of such cations (π-hydrocarbon = olefin, enyl, diene, dienyl, triene, trienyl) towards common nucleophiles, mainly tertiary phosphines [1—3]. However, apart from some kinetic studies with β-diketones [4], aromatic heterocycles [5], activated arenes [3,6], and phosphorus nucleophiles [1—3,7], little quantitative information is currently available concerning nucleophilic reactivities.

We wish to report here preliminary kinetic results concerning the addition of various pyridines and anilines to $[(1\text{-}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]^+$ (I) and $[(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3]^+$ (II) cations (eq. 1 and 2). Synthetic studies of the additions of the parent nucleophiles pyridine and aniline to cation I have been prev-



(1)

(A = H; X = H, 3-Me, 4-Me, 3,5-Me_2, 3-CN)



(2)

(A = OMe; X = H, 2-Me, 3-Me, 4-Me, 4-MeO, 3-Cl, 4-Cl)

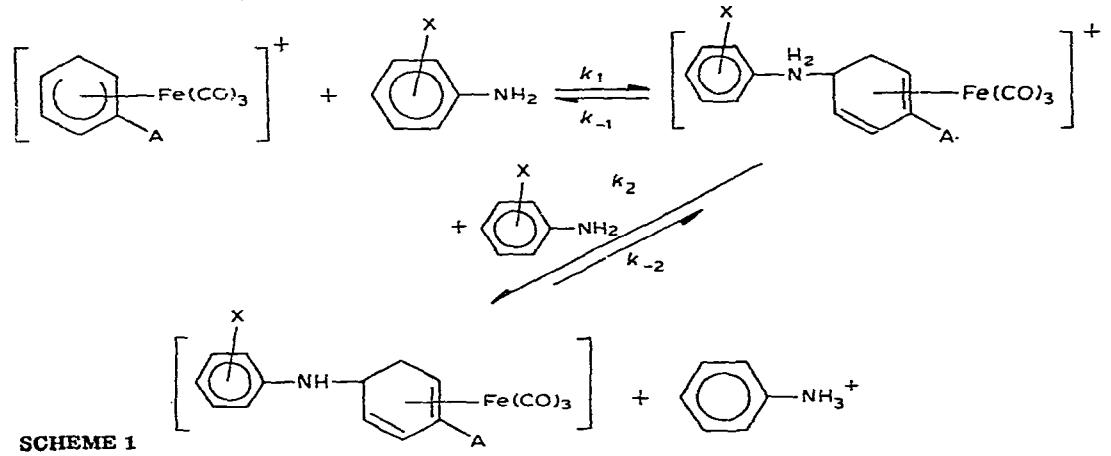
iously reported by others [8,9]. These studies not only extend the range of nucleophile types investigated, but also throw considerable light on the factors important in determining nucleophilicity towards $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ substrates.

Reactions 1 proceed to completion in CH_3CN solvent under the kinetic conditions employed ($[Fe] = 3 \times 10^{-3}$ mol dm^{-3}, $[XC_5H_4N] \geqslant 2 \times 10^{-2}$ mol dm^{-3}), except for X = 3-CN. The rate expression 3 is usually observed, where k corresponds to the second-order rate constant, k_1, for direct addition to the dienyl ring. The only exception is the X = 3-CN case, where eq. 3a is obeyed. Here k_1 refers to the reverse dissociation of the pyridinium adduct.

$$k_{obs} = k[\text{amine}] \quad (3)$$

$$k_{obs} = k_1[\text{amine}] + k_{-1} \quad (3a)$$

The corresponding reactions 2 with anilines are stepwise processes as shown in Scheme 1. For the more basic anilines (X = 4-Me, 4-MeO) the reactions proceed to completion in CH_3CN under the kinetic conditions ($[Fe] = 3.0 \times 10^{-3}$ mol dm^{-3}; $[XC_6H_4NH_2] \geqslant 2 \times 10^{-2}$ mol dm^{-3}). Rate expression (3) is again obeyed. This is most readily rationalised in terms of rapid amine-assisted proton removal ($k_2 \gg k_1, k_{-1}, k_{-2}$), in which case k again refers to k_1 for initial addition to the dienyl ring. In support of this assignment, the k values for reactions of



SCHEME 1

TABLE 1

KINETIC RESULTS FOR ADDITION OF AMINES TO $[(1\text{-}5\text{-}\eta\text{-dienyl})Fe(CO)_3]^+$ CATIONS IN CH_3CN[a]

Cation	Amine	k_1 ($mol^{-1}\,dm^3\,s^{-1}$)
I	pyridine	2130
	4-methylaniline	6470
	2-methylaniline	1270
II	pyridine	425
	4-methylaniline	1010
	2-methylaniline	128
III	pyridine	140
	4-methylaniline	386
	2-methylaniline	71

[a] Temperatures. 0.0°C for pyridine and 4-methylaniline, 10.0°C for 2-methylaniline.

these anilines with cation I are considerably larger than those found for the related reactions of $[(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3]^+$ (II) and $[(1\text{-}5\text{-}\eta\text{-}C_7H_9)Fe(CO)_3]$ (III) (Table 1). Addition to the dienyl rings in these latter cations is predicted to be slower on electronic and steric grounds, respectively. In contrast, for the less basic anilines (X = H, 2-Me, 3-Me, 3-Cl, 4-Cl) the reactions 2 are equilibrium processes even at the highest nucleophilic concentrations employed. For these anilines the two-term rate law 4 is observed. Derivation of a general rate expression for Scheme 1 would be very complex. However, by making the

$$k_{obs} = k'[\text{amine}] + k'' \qquad (4)$$

reasonable assumption that the establishing of equilibrium K_2 occurs much more rapidly than K_1, k' and k'' can be equated to k_1 and $k_{-1}[H^+]/[H^+] + K_2K_a$, respectively. That the experimentally derived k' values do in fact correspond to k_1 is again supported by the decrease in k' along the series I > II > III (Table 1).

The k_1 values summarised in Table 2 for reactions 1 and 2 reveal a very strong dependence on the basicity of the amine nucleophile. This is demonstrated quantitatively by the LFER's obtained on plotting log k_1 vs. pK_a of the amine

TABLE 2

KINETIC RESULTS FOR ADDITION OF SUBSTITUTED (X) PYRIDINES AND ANILINES TO $[(1\text{-}5\text{-}\eta\text{-dienyl})Fe(CO)_3]^+$ CATIONS IN CH_3CN

Cation	X	pK_b	k_1(0°C) ($mol^{-1}\,dm^3\,s^{-1}$)
pyridines (C_5H_4N)			
I	3,5-Me_2	7.83	10400
	4-Me	7.97	8340
	3-Me	8.32	6980
	H	8.77	2130
	3-CN	11.10	8
anilines ($X\text{-}C_6H_4NH_2$)			
II	4-MeO	8.64	1730
	4-Me	8.92	1010
	3-Me	9.27	375
	H	9.40	372
	4-Cl	9.85	82
	3-Cl	10.54	34

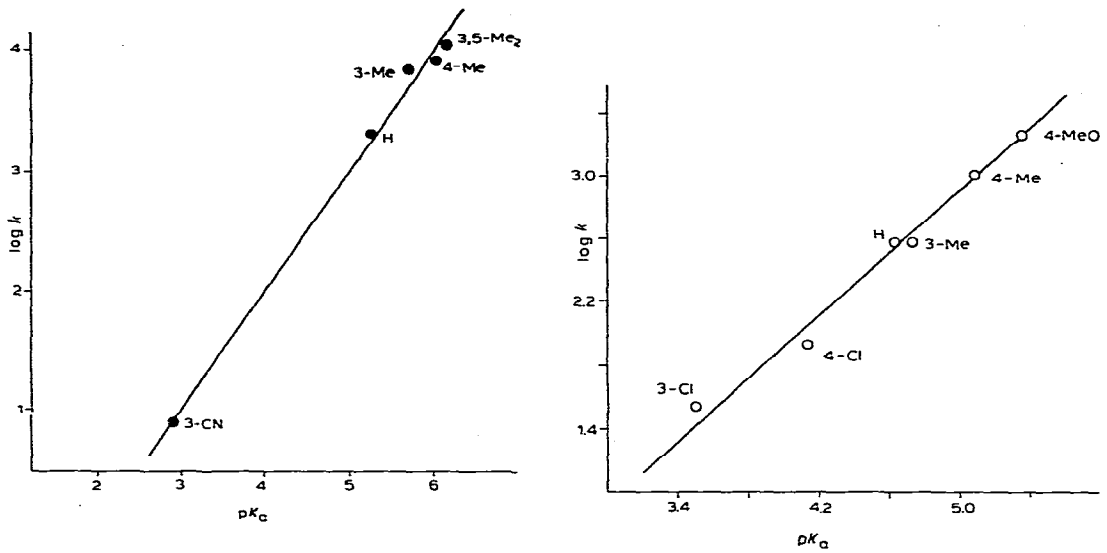


Fig. 1. (a) Plot of log k_1 vs. pK_a of amine conjugate acid for addition of pyridines to [(1-5-η-C_6H_7)Fe-$(CO)_3$]BF_4; (b) Plot of log k_1 vs. pK_a of amine conjugate acid for addition of amines to [(1-5-η-2MeO-C_6H_6)Fe$(CO)_3$]BF_4.

conjugate acid (in water*) (Fig. 1a, b). Reactions 1 and 2 thus obey the Brönsted relationship 5, with slopes, α, of about 1.0 in each case.

$$\log k_1 = \alpha pK_a + \text{constant} \qquad (5)$$

These high slopes contrast with the very low α values of about 0.05 previously found [11] for attack by pyridines and other amines on the very "soft" platinum(II) centre in complexes such as *trans*-[$Pt(py)_2Cl_2$]. For amine attack on moderately "soft" substrates such as alkyl halides α values of about 0.2 have been reported [12]. Interestingly, they are also somewhat larger than the α values of about 0.5 found by Ritchie et al. [13], for amine additions to free carbonium ions. Following the reasoning of Pearson [14], this suggests that the dienyl rings in cations such as I—III are "hard" moieties.

Assignment of a "hard" character to the dienyl groups of cations I—III is consistent with their frequent representation as stabilized carbonium ions, and with the relatively high positive charges calculated [15] to reside on the ring carbons.

We have recently observed [16] a similar strong dependence of k_1 on nucleophile basicity for the related additions of phosphines and phosphites to cations I and II in acetone. Plots of log k_1 vs. the half-neutralisation potentials, Δ(h.n.p.) which have been used [17] as a quantitative measure of basicity for phosphorus nucleophiles, give slopes of −8.72 and −8.49 $volt^{-1}$, respectively. A revealing

*Comprehensive pK_a values for amines are not yet available in CH_3CN. However, a similar but less extended LFER is obtained on plotting log k_1 vs. the basicities of $XC_6H_4NH_2$ (X = H, 4-Me, 4-MeO, 3-Cl) determined in CH_3NO_2 [10].

comparison for present purposes is with *trans*-$[Pt(py)_2Cl_2]$ and methyl iodide substrates. Employing data from ref. 14, slopes of −2.3 and −4.6 volt^{-1}, respectively, are estimated for attack by phosphorus nucleophiles on these "soft" substrates. The much higher slopes for cations I and II are again consistent with their proposed "hard" nature.

In summary, kinetic results for addition of amine and phosphorus nucleophiles to the dienyl cations I—III show a very marked dependence of rate on nucleophile basicity. This suggests a "hard" nature for the dienyl ligands. Further studies are in progress with a variety of neutral and anionic nucleophiles on other $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ complexes to determine if basicity is in general a major factor controlling nucleophilicity.

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