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Kinetics of nucleophilic attack on coordinated organic moieties

XXVI *. An extended nucleophilicity scale for nucleophilic addition to the cation $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$

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Abstract

A nucleophilicity scale is established for the addition of ca. 40 different nucleophiles to the cyclohexadienyl ring of the cation $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$ (I). The factors controlling nucleophilicity towards cation I are discussed, and comparisons made with data for reactions of the nucleophiles with other model organic and inorganic substrates such as MeI and *trans*-$[PtCl_2py_2]$.

Introduction

Rate constants have been reported for the addition of a range of neutral phosphorus, nitrogen and aromatic nucleophiles to the cyclohexadienyl cation $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$ (I) [1–5]. Nucleophilicity constants (N_{Fe}) were calculated [5,6] according to eq. 1, where k_0 is the rate constant for the reference nucleophile $P(OBu^n)_3$, and k_1 is the corresponding rate constant for a particular nucleophile at the same temperature.

$$N_{Fe} = \log_{10}(k_1/k_0) \qquad (1)$$

The limited available data for other $[M(\pi\text{-hydrocarbon})L_n]^+$ electrophiles of varying intrinsic reactivity suggest that relative nucleophilicities (at least for P- and N-donors) are electrophile independent [5,6]. That is, plots of log k_1 vs. N_{Fe} are linear with a slope of near unity for all electrophiles examined to date. Thus, these systems may constitute an important departure from the Reactivity-Selectivity Principle, and provide a close parallel with the behaviour observed by Ritchie [7] for free carbonium ions.

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In order to test this hypothesis, it is necessary to obtain N_{Fe} values for as wide a variety of nucleophiles as possible with the standard organometallic substrate (I). We report here more accurate k_1 values for the reference nucleophile, P(OBu^n)$_3$, and some other P-nucleophiles whose previously reported N_{Fe} values were based on single kinetic determinations. An extension is also made to P(2-CNC$_6$H$_4$)Ph$_2$ and the highly basic amines 1-phenylethylamine and nicotine. Combination with recent data [8] for addition of anions to I provides the first comprehensive nucleophilicity scale for addition to coordinated π-hydrocarbons.

Experimental

Materials

The substrate [Fe(CO)$_3$(1–5-η-C$_6$H$_7$)][BF$_4$] was synthesised and purified by established procedures [9]. Acetone was analytical grade. Acetonitrile (BDH) was distilled in bulk and stored over molecular sieves (grade 3Å). Both solvents were deoxygenated by passing through a stream of nitrogen for 20 min and solutions of the appropriate nucleophile prepared under dinitrogen immediately prior to use.

Kinetic studies

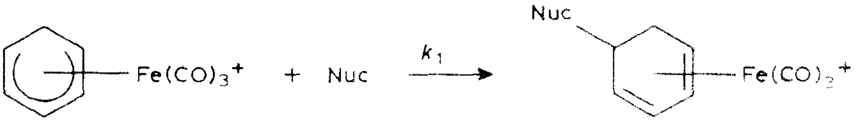
All reactions were studied under psuedo-first-order conditions involving use of a large excess of the nucleophile.

The reaction of I with P(OPh)$_3$ was slow enough to follow under dinitrogen by the IR sampling technique previously described [1]. The decrease of the ν(CO) band of I at 2120 cm^{-1} was monitored, and pseudo-first-order rate constants, k_{obs}, obtained from the slopes of plots of log A_t vs. time. There were linear for ca. two half-lives.

All of the other reactions were rapid, and were monitored at 390 nm with a thermostatted stopped-flow spectrophotometer. At this wavelength a large decrease in absorbance was observed associated with the disappearance of the original complex I. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log($A_t - A_\infty$) vs. time. Such plots were generally linear for at least two half-lives. Each k_{obs} is the average of quadruplicate runs, with an average reproducibility of ±5%.

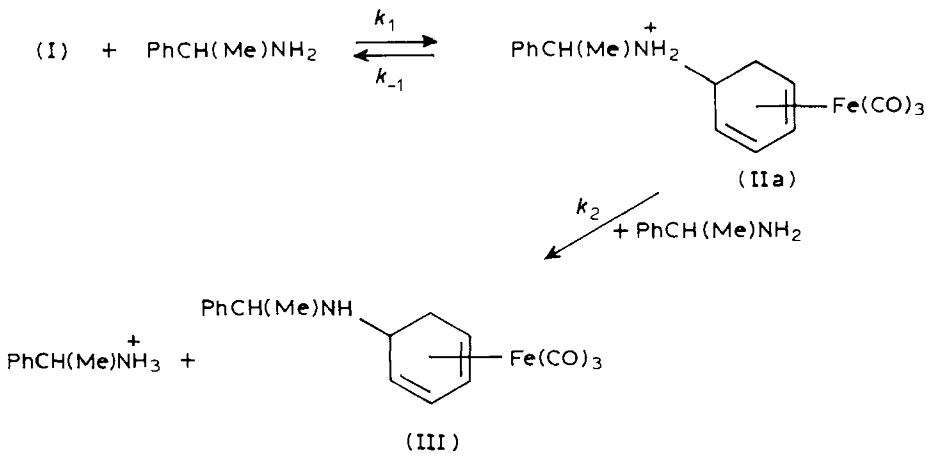
Results and discussion

The isolation and characterisation of the products from the addition of the above P- and N-nucleophiles to cation I are described elsewhere [3,10,11]. In each case *exo*-addition to the cyclohexadienyl ring of I was confirmed [11], giving 5-substituted diene adducts of the type II (eq. 2).



(2)

(I) (II)



Scheme 1

In the case of 1-phenylethylamine, the initial cationic adduct IIa is deprotonated under the kinetic conditions of excess amine to give the neutral adduct III (Scheme 1) [10].

Kinetic results obtained here for reactions (2) are summarised in Table 1. Each of the reactions proceeds to completion under the kinetic conditions employed, and obeys the relationship (3).

$$k_{obs} = k_1[\mathrm{Nuc}] \tag{3}$$

For 1-phenylethylamine, adherence to eq. 3 may be rationalised in terms of the two-step mechanism shown in Scheme 1. Assuming a steady-state concentration for the intermediate IIa, this Scheme leads to the general expression 4. Provided the amine-assisted deprotonation (k_2) is rapid, i.e. $k_2[\mathrm{RNH_2}] \gg k_{-1}$, eq. 4 simplifies to the observed form (eq. 3). Thus, as with the other nucleophiles studied here, the calculated second-order rate constants, k_1, in Table 1 are believed to refer to ring addition.

$$k_{obs} = \frac{k_1 k_2[\mathrm{RNH_2}]^2}{k_{-1} + k_2[\mathrm{RNH_2}]} \tag{4}$$

In no instance was any spectroscopic evidence noted for an intermediate during any of the kinetic studies. This negative observation, together with the general *exo*-configuration established [11] for each of the adducts II, confirms direct *trans*-addition (k_1) to the dienyl ring in each case.

Combination of the results in Table 1 with previous kinetic data [1–5] for other nucleophiles with cation I provides the extended nucleophilicity (N_{Fe}) scale in Table 2, which covers a reactivity range of nine orders of magnitude. Some conclusions may be drawn concerning the factors controlling nucleophilicity towards cation I. A Brönsted plot of log k_1 vs. pK_a for each of the nucleophiles is a scatter diagram (Fig. 1). However, for individual series of nucleophiles such as triarylphosphines, pyridines, and anilines good linear correlations are noted (Fig. 1) [1–3]. The substantial Brönsted slopes, α, of ca. 0.4–0.5 reveal a strong dependence of nucleophilicity upon basicity.

Table 1

Kinetic results for addition of nucleophiles to cation I

Nucleophile	Solvent	T (°C)	10^3[Nuc] (mol dm^{-3})	k_{obs} (s^{-1})	k_1 (mol^{-1} dm^3 s^{-1})
P(4-MeC$_6$H$_4$)Ph$_2$	acetone	20.0	0.480	6.78	
			0.950	12.6	13,700 (750)
			1.43	19.8	
P(2-CNC$_2$H$_4$)Ph$_2$	acetone	20.0	1.50	7.64	
			3.00	15.6	5,330 (10)
			6.00	31.6	
	CH$_3$CN	20.0	3.00	15.1	5,030
P(2-CNC$_2$H$_4$)$_3$	acetone	20.0	8.00	3.20	
			15.0	10.2	
			30.0	19.7	639 (35)
			40.0	28.0	
			80.0	50.0	
P(OBu^n)$_3$	acetone	20.0	6.00	0.646	
			10.0	0.839	
			40.0	3.08	101 (3)
			100	10.1	
			120	12.2	
			150	14.6	
P(OPh)$_3$	CH$_3$CN	20.0	15.0	6.80	
			30.0	14.3	0.047
C$_6$H$_5$CH(Me)NH$_2$	CH$_3$CN	20.0	2.00	64.7	
			3.00	113	36,200
			4.00	147	
Nicotine	CH$_3$CN	0.0	2.00	14.5	
			3.00	25.0	
			5.00	43.9	8540 (130)
			8.00	65.1	
			12.0	100	
		20.0	2.00	38.9	
			3.00	58.6	20,700 (357)
			4.00	78.6	
			5.00	102.4	

Nitrogen nucleophiles are seen to be much less reactive towards cation I than phosphorus donors of the same basicity (Fig. 1). Nevertheless, nitrogen nucleophilicities towards I are markedly enhanced when compared with previous data [12] for reactions of the nucleophiles with MeI or *trans*-[PtCl$_2$py$_2$], which have been extensively studied as model organic and inorganic substrates. Thus, while PPh$_3$ is ca. 10^6 and 20 times more reactive than aniline towards *trans*-[PtCl$_2$py$_2$] and MeI, respectively, it is only ca. twice as reactive as aniline towards I. The relatively low significance of nucleophile polarizability in reaction (2) is dramatically shown by the failure to observe [3] any reaction with AsPh$_3$. These observations are consistent with cation I being a relatively "hard" substrate.

The importance of steric effects in reactions 2 has been previously commented upon [1–3]. For example, the introduction of a 2-methyl substituent onto the

Table 2

Relative nucleophilic reactivities towards cation I at 20 ° C

Nucleophile	Solvent	k_1 ($mol^{-1} dm^3 s^{-1}$)	N_{Fe}	Ref.
$P(2\text{-}MeOC_6H_4)_3$	acetone	680,000	3.83	3
PBu_3^n	acetone	336,000	3.52	3
PEt_2Ph	acetone	155,000	3.19	3
$P(4\text{-}MeOC_6H_4)_3$	acetone	64,200	2.80	3
$H_2NCH(Me)Ph$	CH_3CN	36,200	2.55	This work
$P(4\text{-}MeC_6H_4)_3$	acetone	28,500	2.45	3
nicotine	CH_3CN	20,700	2.31	This work
4-Me aniline	CH_3CN	14,500	2.16 ^{a}	2
$P(4\text{-}MeC_6H_4)Ph_2$	acetone	13,700	2.13	This work
imidazole	CH_3CN	10,800	2.03	5
$H_2NCH(Me)CO_2Et$	CH_3CN	9,130	1.96	16
N_3^-	H_2O	8,630	1.93	8
PPh_3	acetone	7,490	1.87	3
$H_2NCH(Ph)CO_2Et$	CH_3CN	6,500	1.81 ^{a}	16
pyridine	CH_3CN	6,230	1.79 ^{a}	1
$PPh_2(2\text{-}CNC_2H_4)$	acetone	5,330	1.72	This work
$H_2NCH(CH_2Ph)CO_2Me$	CH_3CN	5,000	1.69 ^{a}	16
aniline	CH_3CN	2,780	1.44 ^{a}	2
2-Me-pyridine	CH_3CN	2,150	1.33	1
2-Me-aniline	CH_3CN	2,110	1.32	2
NCS^-	CH_3CN	1,950	1.29	8
$P(4\text{-}FC_6H_4)_3$	acetone	1,570	1.19	3
4-Cl-aniline	CH_3CN	1,470	1.16	2
4-CHO-pyridine	CH_3CN	1,090	1.03	17
$3\text{-}CO_2Me$-pyridine	CH_3CN	980	0.99	17
$P(4\text{-}ClC_6H_4)_3$	acetone	908	0.95	3
$P(2\text{-}CNC_2H_4)_3$	acetone	639	0.80	This work
2-Et-pyridine	CH_3CN	545	0.73 ^{a}	18
4-CN-pyridine	CH_3CN	365	0.56	17
$P(C_6H_{11})_3$	acetone	174	0.24	3
$P(OBu^n)_3$	acetone	101	0.00	This work
$P(OEt)_3$	acetone	46	−0.34	3
$P(OMe)_3$	acetone	30	−0.53	3
$2,6\text{-}Me_2$-pyridine	CH_3CN	28	−0.55 ^{a}	1
$P(2\text{-}MeC_6H_4)_3$	acetone	7.7	−1.12	3
pyrrole	CH_3NO_2	0.16	−2.79	19
indole	CH_3NO_2	0.14	−2.87	19
$P(OPh)_3$	CH_3CN	0.046	−3.34	This work
$4\text{-}Me_2NC_6H_4SnMe_3$	CH_3NO_2	0.0093	−4.04	4
$4\text{-}Me_2NC_6H_4SiMe_3$	CH_3CN	0.00075	−5.13	4

[a] Extrapolated from Arrhenius plot.

pyridine nucleus causes a 10-fold reduction in rate after allowance is made for basicity changes (Table 2) [1]. These steric effects are larger than those found for analogous attack on tetrahedral MeI [13]. This is shown also for the addition of phosphorus nucleophiles to cation I. An excellent correlation is found between log k_1 and the Tolman $\Sigma\chi$ values for thirteen of the P-nucleophiles in Table 2 (Fig. 2). The $\Sigma\chi$ values are a measure of the relative σ-donor and π-accepting ability of the various ligands [13]. The linear correlation ($r = 0.98$) indicates that, despite

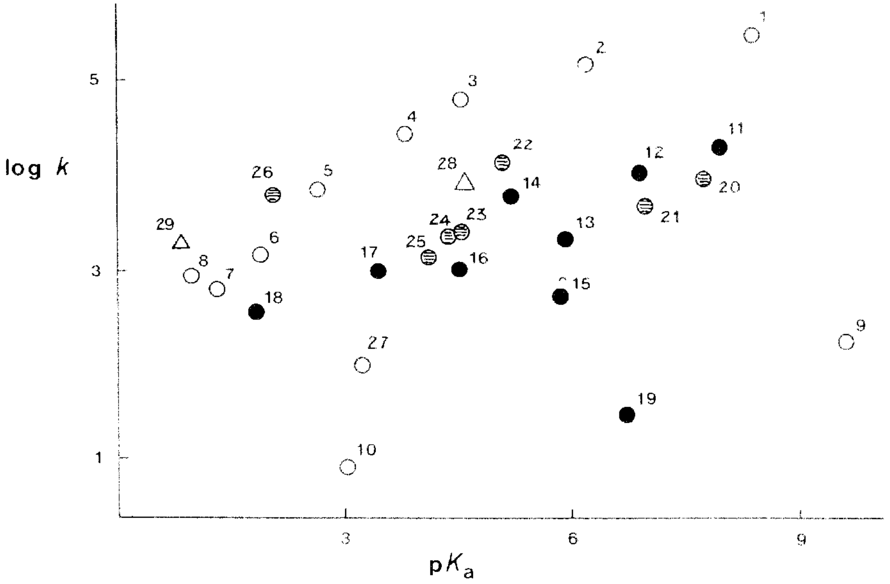


Fig. 1. Plot of log k_1 vs. pK_a for a range of nucleophiles with cation I at 20 ° C. 1, PBu^n_3; 2, PEt_2Ph; 3, $P(4\text{-}MeOC_6H_4)_3$; 4, $P(4\text{-}MeC_6H_4)_3$; 5, PPh_3; 6, $P(4\text{-}FC_6H_4)_3$; 7, $P(2\text{-}CNC_2H_4)_3$; 8, $P(4\text{-}ClC_6H_4)_3$; 9, $P(C_6H_{11})_3$; 10, $P(2\text{-}MeC_6H_4)_3$; 11, nicotine; 12, HIm; 13, 2-Mepy; 14, py; 15, 2-Etpy; 16, 4-CHOpy; 17, 3-CO_2Mepy; 18, 4-CNpy; 19, 2,6-Me_2py; 20, $H_2NCH(Me)CO_2Et$; 21, $H_2NCH(CH_2Ph)CO_2Me$; 22, 4-Me-aniline; 23, aniline; 24, 2-Me-aniline; 25, 4-Cl-aniline; 26, $H_2NCH(Ph)CO_2Et$; 27, $P(OBu)_3$; 28, N_3^-; 29, NCS^-. ○–PR_3, ●–tertiary amines, ⊜–RNH_2, △–anions.

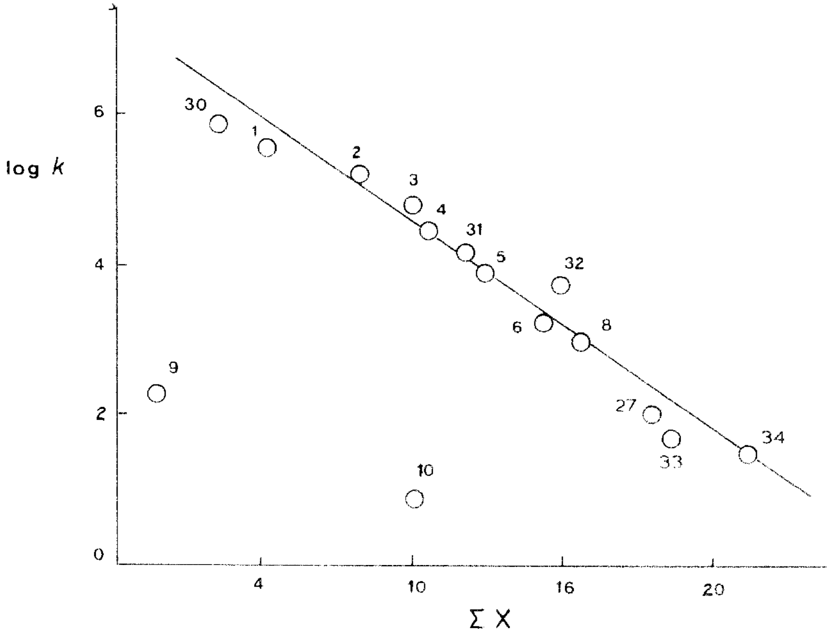


Fig. 2. Plot of log k_1, vs. Tolman $\Sigma\chi$ values for addition of tertiary phosphines and phosphites to I in acetone at 20 ° C, key as in Fig. 1. 30, $P(2\text{-}MeOC_6H_4)_3$; 31, $P(4\text{-}MeC_6H_4)Ph_2$; 32, $PPh_2(2\text{-}CNC_2H_4)_3$; 33, $P(OEt)_3$; 34, $P(OMe)_3$.

significant changes in cone angles along this series (145–107°), similar steric demands occur in the transition state in each case. However, phosphines with very large cone angles do experience severe steric retardation. Thus, $P(C_6H_{11})_3$ and $P(2\text{-}MeC_6H_4)_3$ (with cone angles of 179 and 194°, respectively), show large negative deviations (Δ) of ca. 4 log units below the Tolman plot. That is, their rates are retarded by a factor of ca. 10^4 below that expected on electronic grounds. These steric effects are much larger than for analogous attack on EtI, where $P(C_6H_{11})_3$ shows a deviation (Δ) of only 0.75 log units below its associated Tolman plot [3].

To date, the only anions for which quantitative data are available for attack on I are N_3^- and NCS^- [8]. Qualitative observations [11] indicate that N_3^- is much more reactive than CN^-, which is similar to the observations of Ritchie [7] for free carbonium ions as substrate. Kinetic studies are in progress with a range of other anions in reaction 2 to determine whether the behaviour of cation I closely parallels free carbonium ions. Recent data [3,5,15] suggest such a close relationship for neutral nitrogen and phosphorus nucleophiles.

Acknowledgements

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References

1 T.I. Odiaka and L.A.P. Kane-Maguire, J. Chem. Soc., Dalton Trans., (1981) 1162.
2 L.A.P. Kane-Maguire, T.I. Odiaka, S. Turgoose and P.A. Williams, ibid., (1981) 2489.
3 J.G. Atton and L.A.P. Kane-Maguire, J. Chem. Soc., Dalton Trans., (1982) 1491.
4 G.R. John, L.A.P. Kane-Maguire, T.I. Odiaka, and C. Eaborn, ibid., (1983) 1721.
5 L.A.P. Kane-Maguire, E.D. Honig and D.A. Sweigart, Chem. Rev., 84 (1984) 525, and refs. therein.
6 S.G. Evans, K. Gilmore and L.A.P. Kane-Maguire, J. Chem. Soc., Dalton Trans., in press.
7 C.D. Ritchie, J. Amer. Chem. Soc., 105 (1983) 3573, and refs. therein.
8 J.G. Atton, G. Shaw, and L.A.P. Kane-Maguire, unpublished results.
9 A.J. Birch, P.E. Cross, J. Lewis, D.A. White, and S.B. Wild, J. Chem. Soc. A., (1968) 332.
10 J.G. Atton, L.A.P. Kane-Maguire, P.A. Williams, and G.R. Stephenson, J. Organomet. Chem., 232 (1982) C5.
11 T. Ghazy and L.A.P. Kane-Maguire, unpublished results.
12 R.G. Pearson, H. Sobel and J. Songstad, J. Amer. Chem. Soc., 90 (1968) 319.
13 L.W. Deady, W.L. Finlayson, and O.L. Korytsky, Aust. J. Chem., 32 (1979) 1735.
14 C.A. Tolman, J. Amer. Chem. Soc., 92 (1970) 2953.
15 T.J. Alavosus and D.A. Sweigart, ibid., 107 (1985) 985.
16 P. Jones, L.A.P. Kane-Maguire, and P.A. Williams, J. Chem. Soc., Dalton Trans., submitted.
17 J.G. Atton, L.A.P. Kane-Maguire, and R. Kanitz, J. Chem. Soc., Dalton Trans., submitted.
18 T.I. Odiaka, J. Chem. Soc., Dalton Trans., (1986) 2707.
19 G.R. John, C.A. Mansfield, and L.A.P. Kane-Maguire, J. Chem. Soc., Dalton Trans., (1977) 574, and refs. therein.