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Preliminary communication

Kinetics of nucleophilic attack on coordinated organic moieties

XXIV *. A carbon basicity scale based on the cation $[CpFe(CO)_2(C_2H_4)]^+$

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Abstract

Kinetic and equilibrium studies have been carried out for the addition of a wide range of pyridine and phosphorus nucleophiles to the ethene ligand of the cation $[CpFe(CO)_2(C_2H_4)]^+$. Equilibrium constants determined for these reversible processes are proposed as the basis for a general carbon basicity (pK_c) scale.

Attempts have frequently been made to correlate nucleophilic reactivity towards organic and organometallic substrates with the proton basicity (pK_a) of the nucleophiles [1–3]. For restricted classes of nucleophiles (e.g. pyridines, anilines, phenols, etc), providing no specific steric effects interfere, the Bronsted relationship (1) can be quantitatively obeyed. However, because of the uniquely high charge density of the proton substrate and its inability to enter into π-bonding interactions, it is not surprising that such correlations are often poor.

$$\log K = \alpha pK_a + \text{const.} \qquad (1)$$

It has been suggested [4] that, for reactions at a carbon centre, it would be more appropriate to correlate nucleophilicity with carbon basicity. Several systems have been proposed [4–6] as the basis for a carbon basicity scale. For example, Hine and Weimar [4] have reported basicities for nucleophiles (Y) towards the methyl, hydroxymethyl, phenyl and acetyl cations (R^+), in terms of the equilibrium constant (K_Y^R) for reaction 2. The enthalpy change (ΔH_{RX}) during the reactions of pyridines with methyl- and ethylfluorosulphonates (eq. 3) has similarly been put

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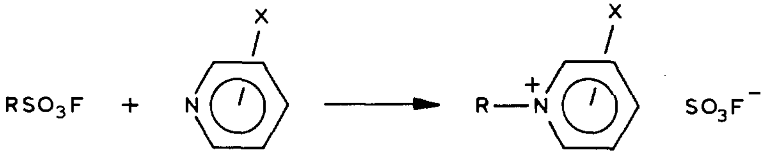
forward as an appropriate measure of pyridine basicity towards carbon [6]. However, an inherent problem if one wishes to correlate a nucleophile-electrophile addition process with such basicities is the influence of the leaving groups (OH^- or SO_3F^-) in reactions 2 and 3.

$$\mathrm{ROH} + \mathrm{Y} \overset{K_Y^R}{\rightleftharpoons} \mathrm{RY}^+ + \mathrm{OH}^- \qquad (2)$$


(3)

In order to overcome these difficulties, we now propose reaction 4 as a suitable basis for a general carbon basicity scale. This reaction, which is reversible for a wide range of nitrogen, oxygen, and phosphorus nucleophiles, involves simple addition of the nucleophile (Y) to a coordinated ethene carbon atom [7–9]. *Trans*-approach of the nucleophile to the planar sp^2 carbon atom minimises steric interactions. Kinetic studies reveal the general rate law, $k_{obs} = k_1[Y] + k_{-1}$ [8,9].

$$[\mathrm{CpFe(CO)_2(C_2H_4)}]^+ + \mathrm{Y} \underset{K_c}{\rightleftharpoons} [\mathrm{CpFe(CO)_2(C_2H_4 \cdot Y)}]^+ \qquad (4)$$

Equilibrium constants (K_1) for reactions 4, determined from in situ IR experiments at 20 °C, are shown in Table 1 for various pyridine and phosphorus nucleophiles. These values agree closely with those ($K_1 = k_1/k_{-1}$) obtained from kinetic studies [9]. The reverse dissociation process in eq. 4 is a direct carbon analogue of the dissociation (K_a) of a protonic acid, HY. We shall employ the term K_c for this dissociation equilibrium ($K_c = k_{-1}/k_1$), which may be used as a quantitative measure of the carbon basicity of Y.

The pK_c values given in Table 1 for various substituted pyridines correlate closely with the corresponding pK_a values (Fig. 1). The correlation slope of 0.88 shows that, thermodynamically speaking, the carbon substrate $[\mathrm{CpFe(CO)_2(C_2H_4)}]^+$

Table 1

Equilibrium constants (K_1) for reactions 4 in acetone at 20 °C, and associated pK_c values.

Y	K_1	2 + pK_c (acetone)	pK_a (H_2O)
3,4-Me_2py	810	4.91	6.48
3,5-Me_2py	450	4.65	6.14
4-Mepy	380	4.58	6.03
3-Mepy	190	4.28	5.67
4-Phpy	150	4.18	5.35
py	71	3.85	5.21
4-CHOpy	1.3	2.11	4.52
4-CO_2Mepy	0.52	1.72	3.49
4-CNpy	0.070	0.85	1.86
$P(OBu^n)_3$	200	4.30	3.3
$P(2\text{-}CNC_2H_4)_3$	1100	5.04	1.37

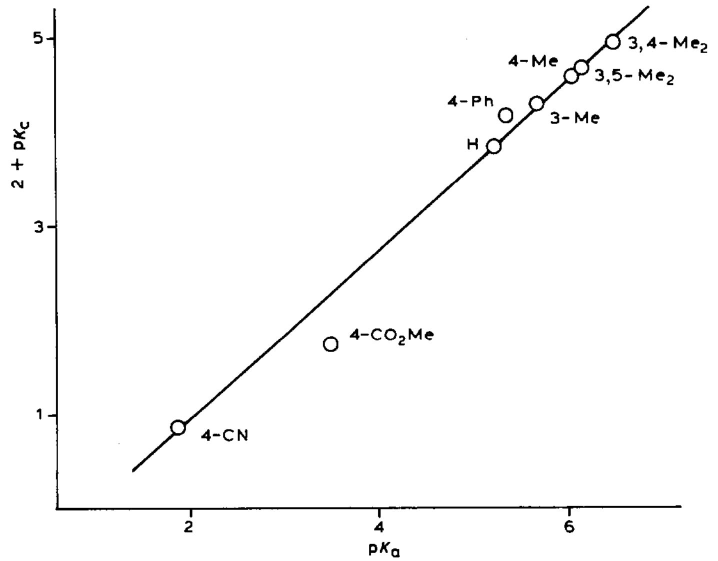


Fig. 1. Plot of pK_c values for reaction 4 in acetone vs pK_a (in water) for various substituted pyridines.

(I) is almost as sensitive as a proton towards electronic changes in Y. However, phosphorus nucleophiles are seen from Table 1 to be much more basic towards the carbon substrate (I) than to a proton. For example, while $P(OBu^n)_3$ and 4-$CO_2MeC_5H_4N$ have similar pK_a values, the pK_c value of the phosphite is 2.6 log units higher than that of the substituted pyridine. This marked difference in the carbon basicities of *P*- and *N*-nucleophiles is reflected in the generally higher reactivity of phosphorus reagents towards carbon substrates compared with nitrogen donors of similar proton basicity.

Another useful feature of reaction 4 is that pK_c values can be readily measured in a wide variety of solvents. For example, pK_c values recorded in acetonitrile for substituted pyridines are generally ca. 0.2 log units lower than those shown in Table 1.

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