Measurement of pK_a values for Phosphonium Salts *via* the Kinetics of Proton Transfer to an Electrogenerated Base

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pK_a values have for the first time been measured for common phosphonium ions, including butyl-, allyl-, prop-2-ynyl- and benzyl-triphenylphosphonium, by comparison through a linear Brønsted plot of their rates of proton transfer to an electrogenerated base with those involving carbon acids of known acidity.

Few measurements have been made of pK_a values for phosphonium salts yet their deprotonation to form ylids is much used in synthesis and is a key step in the Wittig reaction. It is only for the most acidic phosphonium salts, such as β-ketophosphonium salts, that pK_a values have been re-corded.[1] Comparisons[2] of the relative acidities of phosphonium salts, by the transylidation method, do not give quantitative information for salts less acidic than benzyltri-phenylphosphonium, recorded only as p$K_a \geqslant 11$. Measure-ment[3] of rates of hydrogen–deuterium exchange serve only to

Table 1. Kinetics[a] of proton transfer between $(1)^{2-}$ and carbon acids.

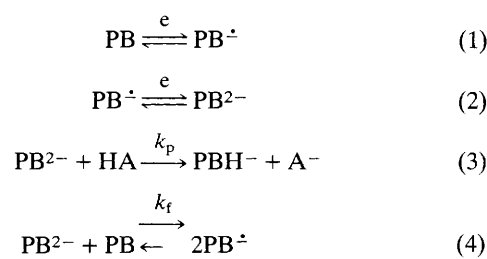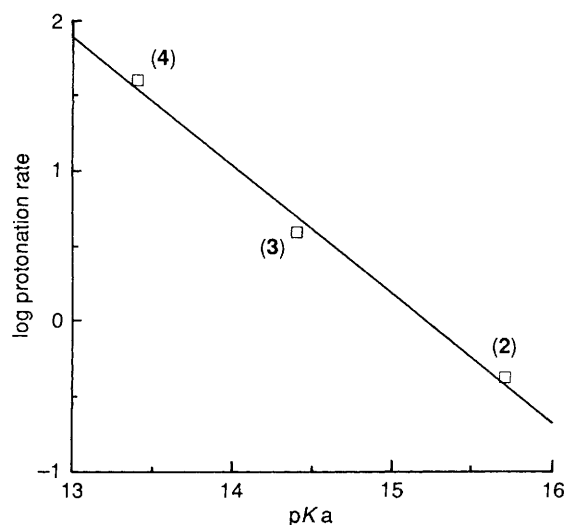| Carbon acid	pK_a value		
(HA)	Ref. 8	Interpolation	k_p/s^{-1}
(2)	15.7		0.41 ± 0.02
(3)	14.4		3.88 ± 0.50
(4)	13.4		40.2 ± 5.1
(5)[b]		15.4	0.68 ± 0.08
(6)[b]		14.3	6.71 ± 0.29
(7)[b]		13.9	$[25.2 \pm 4.5]^{c}$
(8)[b]		13.6	29.5 ± 5.39
(9)[b]		$(12.7)^{d}$	147 ± 10
(10)[b]		$(12.6)^{d}$	182 ± 29

[a] Double potential step chronoamperometry at Pt disc cathode, DMSO/Bu$_4$NClO$_4$ (0.1 M), 25 ± 0.1 °C; probase concentration 2×10^{-3} M; carbon acid in 20-fold excess. Values of k_p calculated by the Schwarz–Shain method[7] assuming steps (1)—(3) of Scheme 1, *i.e.*, no allowance for reproportionation.[6] [b] Phosphonium bromides. [c] Statistically corrected, *i.e.*, twice the measured value. [d] By minor extrapolation (see Figure 1).
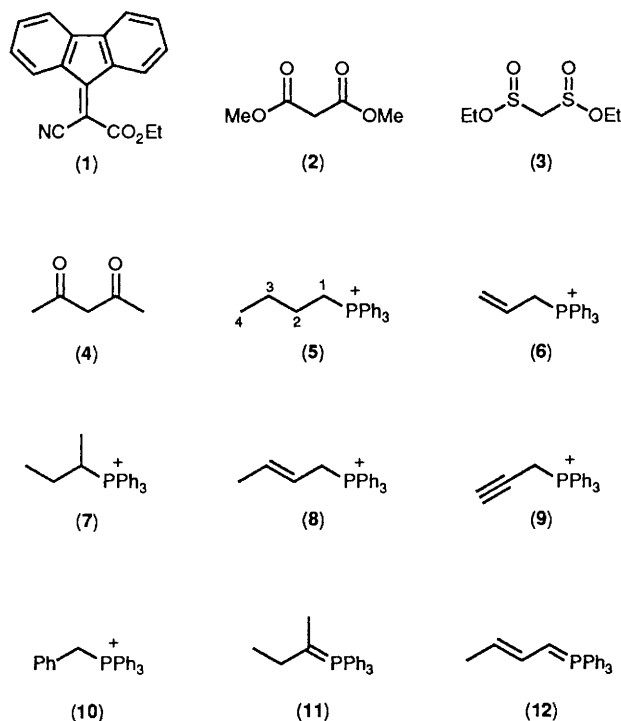
show that the kinetic acidity of phosphonium ions is lower than that of the corresponding nitroalkanes and pK_a values were not derived.

We report herein on the precise measurement, using double potential step chronoamperometry, of kinetic acidities of several representative phosphonium salts which may be compared through the Brønsted relationship with the known pK_a values of other carbon acids. This appears to be the first direct and precise measurement of the acidity of common phosphonium salts.

Bases may often be conveniently generated cathodically;[4] such electrogenerated bases (EGBs) are the reduced form of probases (PBs) and are typically radical-anions or -dianions.

$$PB \overset{e}{\rightleftharpoons} PB^{\cdot -} \tag{1}$$

$$PB^{\cdot -} \overset{e}{\rightleftharpoons} PB^{2-} \tag{2}$$

$$PB^{2-} + HA \overset{k_p}{\longrightarrow} PBH^- + A^- \tag{3}$$

$$PB^{2-} + PB \overset{k_f}{\underset{\longleftarrow}{\longrightarrow}} 2PB^{\cdot -} \tag{4}$$

Scheme 1

Figure 1. Brønsted plot (data from Table 1).

Electroanalytical techniques, such as cyclic voltammetry and double potential step chronoamperometry, may be used to measure the rates of subsequent reactions of such intermediates. Thus Kinlen *et al.*[5] were the first to measure the rates of reaction of EGBs (substituted azobenzene radical anions) with carbon acids of established pK_a. They found a linear Brønsted relationship between the pK_a values and rates of proton transfer. In a recent examination[6] of the reactivity of dianions generated cathodically from fluoren-9-ylidene derivatives, we developed a convenient and reliable double potential step chronoamperometric method for measuring rates of proton transfer between the dianions and carbon acids. In these cases a competing reaction is reproportionation [k_f step (4) in Scheme 1] but it was shown[6] that the slower proton transfer rate (k_p) can be extracted by computer simulation of the current/time transients assuming the complete reaction mechanism given in Scheme 1. Relative rates of proton transfer may, even in these cases, be reliably measured by the Schwarz–Shain method.[7]

In dimethyl sulphoxide (DMSO) at 25 °C and for the case where the PB is compound (1) a linear Brønsted plot is obtained for log k_p *vs.* pK_a values for the carbon acids (2)—(4) (Figure 1); the pK_a values are those determined by Bordwell and his co-workers[8] for the same solvent and temperature. The Brønsted plot has a slope of 0.86 and a correlation coefficient of 0.996. A 20-fold excess of carbon acid is used and therefore k_p is expressed as a pseudo-first order coefficient; the experimental method used has been fully described.[6] Similarly, rate coefficients for proton transfer between the phosphonium salts (5)—(10) and the dianion of (1) may be measured. Earlier,[9] qualitative work, has estab-

lished that the result of such a reaction involving *in situ* formation of EGBs is ylid formation. The pK_a values may be obtained by interpolation using Figure 1 except for those of the salts (9) and (10) when minor extrapolation is required. The results of all of these measurements are summarised in Table 1.

The pK_a values for the phosphonium salts (5)—(10), listed in Table 1, represent kinetic acidities determined for reaction with just one base and in DMSO at 25 °C. Somewhat different values might well be obtained should a different base be employed or should the comparison be made with carbon acids other than those of type (2)—(4). However, in the absence of direct measurement of thermodynamic acidities the values in Table 1 are the best and only measurements to date.

The acidity increase from (5) to (6) is as expected and it is not surprising that the most acidic phosphonium salts are (9) and (10). The relatively high acidities of (7) and (8) are not easily explained in terms of carbanion stabilisation at C-1. However representation of the ylid as involving a carbon–phosphorus double bond, in keeping with the reduced bond length on ylid formation,[10] may suggest an explanation. The conjugate base of (7) may then be best depicted as (11) and that of (8) as (12). The factors whereby highly substituted alkenes and polyenes are stabilised then come into play *e.g.*,

the extra alkyl substitution would stabilise the deprotonation product of (7) *vis à vis* (6).

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