Conjugation and proton exchange equilibria. Heteroconjugation constants in substituted phenol–piperidine systems in acetonitrile

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It has been shown by mathematical transformations that the final equations and expressions required for determining equilibrium concentrations of major species in HA + B systems are analogous to those used previously for HA + A_1^- systems. Heteroconjugation constants $\vec{K}_{AHB} = [AHB]/([HA][B])$ for eight substituted phenol (HA)–piperidine (B) systems in acetonitrile (AN) were determined from emf measurements. A fairly linear dependence between log $\vec{K}_{AHB}$ and $\Delta pK_a^{AN} = pK_{BH^+}^{AN} - pK_{HA}^{AN}$ was observed with a slope of 0.52. The $[K_{AHB}^2/(K_{AHA^-}\ K_{BHB^+})]_{at\ \Delta pK_a = 0}$ quotient appeared to be much greater than $[K_{AHA_1^-}^2/(K_{AHA^-}\ K_{A_1HA_1^-})]_{at\ \Delta pK_a = 0}$ calculated from results obtained previously for HA + A_1^- type systems. From this fact it has been concluded that the formation of AHB type complexes (relative to the AHA^- and BHB^+ type complexes) is likely to be favoured by their overall neutrality ensuring weaker peripheral interactions.

1. Introduction

Quantitative treatment of protonic hetero systems is one of the most important subjects in chemistry. In the HA + B systems in polar protophilic solvents, such as water or methanol, one commonly assumes the occurrence of only a Brønsted type equilibrium (1) (referred to as a proton exchange equilibrium).

$$HA + B \rightleftharpoons A^- + BH^+ \quad (1)$$

Proton exchange may result from direct interaction (*via* the intermediate state AHB) or from two exchange reactions with the participation of solvent molecules [equilibria (2) and (3)].

$$HA + S \rightleftharpoons A^- + SH^+ \quad (2)$$

$$B + SH^+ \rightleftharpoons BH^+ + S \quad (3)$$

In solvents of weak proton-donating and/or weak proton-accepting properties other equilibria become significant. Among them, homoconjugation equilibria (4) and (5), and

$$HA + A^- \rightleftharpoons AHA^- \quad (4)$$

$$BH^+ + B \rightleftharpoons BHB^+ \quad (5)$$

heteroconjugation equilibria (6) and (7), are the most important and in the light of previous studies[1] seem, in general, fully competitive with each other unless steric effects or a type of hydrogen bridge are governing.

$$HA + B \rightleftharpoons AHB \quad (6)$$

$$BH^+ + A^- \rightleftharpoons AHB \quad (7)$$

While the homoconjugate systems have been rationalised,[2] heteroconjugate systems appear to be much more complicated. The heteroconjugation constants for molecular protonic hetero systems have so far been determined essentially by methods based on conductometric measurements.[3–7] The fundamental problem in the successful application of these measurements arises from the fact that the mixture obtained after dissolution of the salt BH^+A^- always contains not only BH^+ and A^-, as required by Ostwald's dilution law but also contains at least HA, B, AHA^-, BHB^+, AHB *etc.* There is also no reason why infinite dilution should lead to a specific state in which only BH^+ and A^- are present. The equilibrium constant value of $[A^-][BH^+]/([HA][B])$ for a given protonic hetero system HA + B does not allow for this. Consequently, there are many unknowns and it is very easy to violate the chemical equilibrium law or the mass balance for fundamental equilibria (1)–(7). Despite numerous attempts, spectrophotometric methods of determining heteroconjugation constants have not been successfully developed. Most of them are still at the stage of the Benesi–Hildebrand method[8] which is based on eqn. (8).

$$C_{HA} = [HA] + [AHB] \quad (8)$$

For systems of sufficiently high ΔpK_a the equilibrium concentrations of the species ignored ($[BH^+]$ or $[A^-]$) may be a hundred times higher than those taken into account ([HA] or [AHB]). Therefore the obtained results may be of little value. The method which seems to offer a reasonable solution to the problem of heteroconjugation is one based on emf measurements. A solution given previously[9] fulfils the two fundamental requirements: the law of the chemical equilibrium constant in respect to equilibria (1)–(7) and the mass balance rule for the most significant species. It was, however, designed for anionic systems (HA + A^-). In the respective expressions for such systems, activity coefficients appear in different positions than in the expressions for molecular systems. This could give the impression that the same method of calculation cannot be directly applied to molecular systems.

The major objective of this work was to show transformations illustrating that the same method of calculation may be applied to molecular hetero systems. An important aim of this

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work was to study model systems for which a transition through the point corresponding to $\Delta pK_a = 0$ is readily accomplished. Finally, our concern was focused on whether, by comparing heteroconjugation constants and parent homoconjugation constants, one can draw any conclusions about specific differences between ionic and molecular hetero systems.

2. Derivation of expressions and equations for molecular protonic hetero systems

The seven fundamental equations are (9)–(15) where C_{HA} and

$$K_{HA} = \frac{a_{H^+}[A^-]y_{A^-}}{[HA]} \quad (9)$$

$$K_{BH^+} = \frac{a_{H^+}[B]}{[BH^+]y_{BH^+}} \quad (10)$$

$$K_{AHA^-} = \frac{[AHA^-]y_{AHA^-}}{[HA][A^-]y_{A^-}} \quad (11)$$

$$K_{BHB^+} = \frac{[BHB^+]y_{BHB^+}}{[B][BH^+]y_{BH^+}} \quad (12)$$

$$C_{HA} = [HA] + [BH^+] + [AHA^-] + [BHB^+] + [AHB] + [SH^+] \quad (13)$$

$$C_{HA} = [HA] + [A^-] + 2[AHA^-] + [AHB] \quad (14)$$

$$C_B = [BH^+] + [B] + 2[BHB^+] + [AHB] \quad (15)$$

C_B denote the analytical concentrations of the proton donor HA and proton acceptor B respectively. Eqns. (13)–(15) represent the mass balance rule for protons, A moieties and B moieties respectively. For simplicity, let us assume that all activity coefficients y are equal to a so called medium activity coefficient $y_\pm$ given in eqn. (16).

$$y_{A^-} = y_{BH^+} = y_{AHA^-} = y_{BHB^+} = y_\pm \quad (16)$$

Should any reasonable method of calculating activity coefficients for such large ions appear, we have a use for it. Also, to simplify the notation, let us neglect $[SH^+]$ in eqn. (13), as in aprotic solvents it is several orders of magnitude lower than any other equilibrium concentration taken into account. By multiplying eqn. (13) by 2 and subtracting eqns. (14) and (15) one obtains eqn. (17). Substitution of $K_{HA}[HA]/(a_{H^+}y_\pm)$ for $[A^-]$ and $K_{BH^+}[BH^+]y_\pm/a_{H^+}$ for [B] yields eqn. (18).

$$C_{HA} - C_B = [HA] - [A^-] + [BH^+] - [B] \quad (17)$$

$$C_{HA} - C_B = [HA]\left(1 - \frac{K_{HA}}{a_{H^+}y_\pm}\right) + [BH^+]\left(1 - \frac{K_{BH^+}y_\pm}{a_{H^+}}\right) \quad (18)$$

Unlike the situation in the analogous equation for the $HA + A_I^-$ systems, the second term contains the activity coefficient in the numerator and not in the denominator. One should notice, however, that the respective expressions for K_{HA} and K_{BH^+} as functions of the measured values of E_{AHA^-} and E_{BHB^+} are as shown in eqns. (19) and (20), where E_{AHA^-} is the

$$K_{HA} = y_\pm\, 10^{(E_{AHA^-} - E_0)/s} \quad (19)$$

$$K_{BH^+} = \frac{10^{(E_{BHB^+} - E_0)/s}}{y_\pm} \quad (20)$$

emf of the cell containing equimolar amounts of HA and $Bu_4N^+A^-$, E_{BHB^+} is the emf of the cell containing equimolar amounts of BH^+ ClO_4^- and B, E_0 is the standard potential of the glass electrode and s is the slope of the glass electrode calibration curve. After substituting these expressions into eqn. (18), the medium activity coefficient cancels out. Moreover, by substituting $10^{(E - E_0)/s}$, where E is the measured emf of the cell, for a_{H^+} one obtains eqn. (21). After rearranging, the equation

$$C_{HA} - C_B = [HA]\left(1 - \frac{10^{(E_{AHA^-} - E_0)/s}}{10^{(E - E_0)/s}}\right) + [BH^+]\left(1 - \frac{10^{(E_{BHB^+} - E_0)/s}}{10^{(E - E_0)/s}}\right) \quad (21)$$

takes the form given in eqn. (22) where p is given in eqn. (23) and r in eqn. (24).

$$[BH^+] = p[HA] + r \quad (22)$$

$$p = \frac{10^{E_{AHA^-}/s} - 10^{El/s}}{10^{El/s} - 10^{E_{BHB^+}/s}} \quad (23)$$

$$r = \frac{(C_{HA} - C_B)10^{El/s}}{10^{El/s} - 10^{E_{BHB^+}/s}} \quad (24)$$

Thus, parameters p and r as well as further transformations leading to the final equilibrium concentrations of particular species are exactly analogous to those for the $HA + A_I^-$ systems given previously.[9] This means that every $K_{A_IHA_I^-}$ given in ref. 9 should be replaced by K_{BHB^+} and every $E_{A_IHA_I^-}$ should be replaced by E_{BHB^+}. The final equilibrium concentration of HA is expressed by eqn. (25)

$$[HA] = \frac{-b - \sqrt{b^2 - 4ac}}{2a} \quad (25)$$

where

$$a = p^2\, K_{BHB^+}\, 10^{E_{BHB^+}/s} - K_{AHA^-}\, 10^{E_{AHA^-}/s} \quad (26)$$

$$b = 2p\, r\, K_{BHB^+}\, 10^{E_{BHB^+}/s} - 10^{E_{AHA^-}/s} + p\, 10^{El/s} \quad (27)$$

$$c = r^2\, K_{BHB^+}\, 10^{E_{BHB^+}/s} + r\, 10^{El/s} \quad (28)$$

Knowing this, one can calculate the remaining equilibrium concentrations from eqns. (10)–(15), (22) and finally the sought-after heteroconjugation constants in eqns. (29) and (30).

$$\vec{K}_{AHB} = \frac{[AHB]}{[HA][B]} \quad (29)$$

$$\overleftarrow{K}_{AHB} = \frac{[AHB]}{[BH^+][A^-]y_\pm^2} \quad (30)$$

3. Experimental

Acetonitrile and substituted phenols were purified as before.[10] Substituted phenolates were prepared and analyzed as previously described.[11]

Piperidine (Serva, pure) was dried over KOH for 24 hours and distilled through a Vigreaux column at a rate of ~1 cm^3 min^{-1}. The middle fraction of bp 106 °C was used for preparing a 1.00 M stock solution in acetonitrile. This solution was used for the careful (protected from atmospheric CO_2) preparation of the final solutions for studies.

Piperidinium perchlorate was prepared by mixing equimolar quantities of perchloric acid in an ethanol–water solution and piperidine in ethanol. Solvents were then evaporated under reduced pressure and as an azeotrope with benzene. The final

Table 1 Melting points and elemental analyses of some of the studied piperidinium phenolates

Piperidinium salt	Melting point/°C	C (%) Found	C (%) Calc.	H (%) Found	H (%) Calc.	N (%) Found	N (%) Calc.	V_u/V_t [a]
2,6-Dichlorophenolate	119–120.5	53.21	53.24	6.18	6.09	5.40	5.64	0.998
2,4,6-Trichlorophenolate	138–139.5	46.62	46.75	4.90	4.95	4.74	4.96	0.988
2,4,6-Tribromophenolate	170–171	31.79	31.76	3.36	3.39	3.06	3.37	0.989
Pentachlorophenolate	230–231	37.72	37.59	3.46	3.44	3.87	3.96	1.001
2,4-Dinitrophenolate	163–164.5	49.39	49.07	5.74	5.61	15.51	15.61	0.992
Hydrogen-bis(4-nitrophenolate)	104–105.5	56.17	56.19	5.79	5.82	11.56	11.56	0.990
Perchlorate	149–150	32.41	32.36	6.43	6.51	7.01	7.55	—

[a] V_u/V_t denotes the ratio of the volume of perchloric acid solution used to the theoretical volume expected for pure salt.

product was crystallized from ethyl acetate (p.p.a. P.O.CH. Gliwice).

Crystal heteroconjugates of piperidine with 2,4,6-tribromo-, 2,4,6-trichloro-, 2,6-dichloro-, 2,4-dinitro-, 2,6-dinitro- and pentachlorophenol were obtained by mixing equimolar quantities of piperidine and the corresponding phenol in methanol, evaporation of sufficient quantity of solvent and crystallization in a refrigerator. In some cases (*e.g.* during crystallization of piperidinium pentachlorophenolate) the mixtures of methanol or ethanol with ethyl acetate appeared to be more efficient. When 4-nitrophenol was used as a reagent, instead of its simple heteroconjugate (AHB), piperidinium hydrogen-bis(4-nitrophenolate) BH^+ AHA^- crystallized out. The purity of these compounds was examined by potentiometric titration with 0.0938 M perchloric acid in acetic acid and the elemental analysis was performed on a Carlo Erba 1106 Elemental Analyzer (Table 1).

Potentiometric measurements were carried out at 298 ± 0.1 K using the same equipment and standards as before,[9,10] three times for each system studied. The glass electrode (E_0 = 1092.5 mV, s = 59.75 mV per pH unit) was calibrated in buffer solutions containing 2,6-dinitrophenol and tetrabutylammonium 2,6-dinitrophenolate. In a single measurement, in order to determine the heteroconjugation constant, 20.00 cm^3 of a 1.00×10^{-3} M solution of piperidine (B) in acetonitrile was placed in the cell and the appropriate precalculated volumes of a titrant containing 1.10×10^{-2} M substituted phenol and 1.00×10^{-3} M piperidine in acetonitrile were added.

In an auxiliary measurement to determine the homoconjugation constant for the piperidine–piperidinium ion system, 20.00 cm^3 of 1.00×10^{-3} M piperidinium perchlorate in acetonitrile was placed in the cell and appropriate precalculated volumes of a titrant containing 1.10×10^{-2} M piperidine and 1.00×10^{-3} M piperidinium perchlorate in acetonitrile were added. For calculations of the relatively low homoconjugation constant K_{BHB^+} (according to the method analogous to that applied for AHA^- type conjugates[2,10]) the average value of the four measurements was used. The emf values E_{AHA^-} and E_{BHB^+} necessary for further calculations were determined on the same day as the emf values for the corresponding titration points.

4. Results and discussion

Table 1 contains melting points and elemental analyses of the seven salts which appeared to be the easiest to prepare in a pure state. The preparation of simple 4-nitrophenolate salt of piperidinium ion was totally unsuccessful, indicating a strong tendency of the 4-nitrophenolate ion towards homoconjugation. Presumably, the crucial reason for this failed preparation was the fact that the piperidinium ion is a stronger proton donor in non-aqueous solvent ($pK^{AN}_{BH^+}$ = 19.1) than 4-nitrophenol (pK^{AN}_{HA} = 21.1$_5$),[10] so it simply could not survive in the solution at a reasonable equilibrium concentration to force the precipitation of the simple salt. Presumably, the same problem occurred during the attempted preparation of the piperidinium 2,6-dichlorophenolate. In this particular case, however, the preparation of the homoconjugate salt was unsuccessful because of the steric effect of the two chlorine substituents in *ortho* positions. We think that the problems mentioned above may serve as a useful guide for those who are interested in preparing analogous classes of compounds.

Table 2 Heteroconjugation constants (log $\vec{K}_{AHB}$) for the substituted phenol (HA)–piperidine (B) systems in acetonitrile determined by electrometric methods

Nr	Substituted phenol	ΔpK^a	log $\vec{K}_{AHB}$ [b]	Standard deviation for log $\vec{K}_{AHB}$
1	2,6-Dichloro-	−2.7	2.9_2	0.10
2	4-Nitro-	−2.05	3.3_4	0.07
3	2,4,6-Trichloro-	−1.3	3.6_1	0.08
4	2,4,6-Tribromo-	−0.8	4.1_1	0.04
5	2,5-Dinitro-	0.7	4.3_3	0.18
6	Pentachloro-	1.5	5.1_9	0.04
7	2,4-Dinitro-	2.8	5.3_2	0.08
8	2,6-Dibromo-4-nitro-	4.1	6.8_0	0.15

[a] Values based on pK^{AN}_{HA} of phenols determined in ref. 10 and pK_{BH^+} = 19.1 (this work). [b] For each system with a negative ΔpK^{AN}_a value, log $\vec{K}_{AHB}$ has been calculated as the average of those corresponding to the 20 experimental points of lowest log (C_{HA}/C). For each system with a positive ΔpK^{AN}_a value, log $\vec{K}_{AHB}$ has been calculated as the average of those corresponding to the 20 experimental points of highest log (C_{HA}/C_B) (see text).

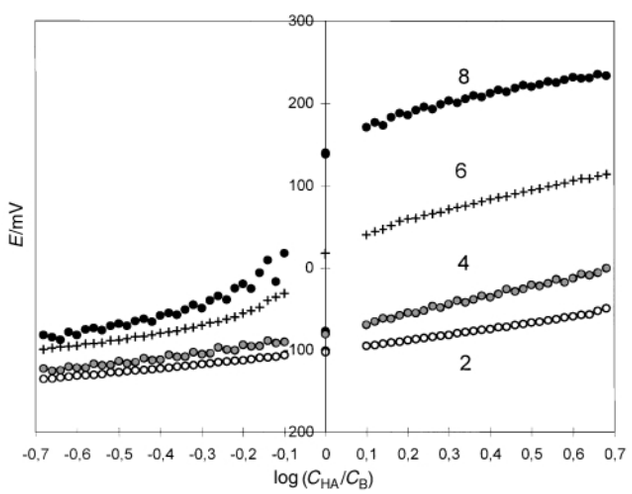

Fig. 1 Potentiometric titration points for selected substituted phenol–piperidine systems in acetonitrile. The results for each particular system are represented by three independent series of measurements. The numbering refers to that given in Table 2.

Fig. 1 shows the commonly observed dependence between measured emf and log (C_{HA}/C_B) for four selected systems with different ΔpK^{AN}_a. As could be expected, the slope of the tangent to the curve at log (C_{HA}/C_B) = 0 is generally steeper for systems

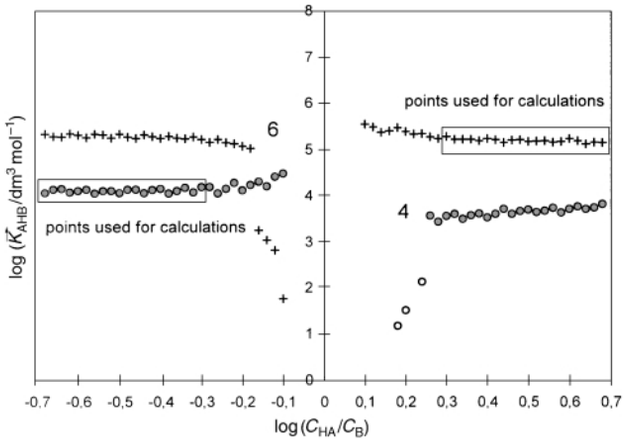

Fig. 2 Experimentally determined log $\vec{K}_{AHB}$ values for particular titration points in selected substituted phenol–piperidine systems in acetonitrile as a function of log (C_{HA}/C_B). The numbering refers to that given in Table 2.

of larger ΔpK_a^{AN}. Since homoconjugation in the piperidine–piperidinium ion system is relatively weak, no indication of any additional jumps in E at log (C_{HA}/C_B) < 0 were observed. The homoconjugation constant determined for the piperidinium ion–piperidine system in this work (log $K_{BHB^+} = 1.6$) and the previously reported homoconjugation constants for substituted phenol–phenolate systems [10] were used along with the measured emf values for equimolar HA + A^- and BH^+ + B mixtures to calculate equilibrium concentrations of all species of interest.

An example of the log $\vec{K}_{AHB}$ determination for pentachlorophenol (HA)–piperidine (B) system

(a) The values from separate determinations using the same measuring system ‡ are s (mV per pH unit) = 59.75 [this work], log $K_{AHA^-} = 2.6$ (ref. 10) and log $K_{BHB^+} = 1.6$ [this work].

(b) The values measured on the same day as the main determination are $E_{AHA^-} = 42.1_0$ mV,§ $E_{BHB^+} = -44.5_4$ mV, $V_0 = 20.00$ cm^3, $V_t = 3.55$ cm^3 and $E = 60.5$ mV, where V_0 is the initial volume of the titrated solution ($C_B = 1.00 \times 10^{-3}$ M), V_t is the volume of titrant ($C_{HA} = 1.10 \times 10^{-2}$ M, $C_B = 1.00 \times 10^{-3}$ M) and E is the emf of the cell after addition of V_t cm^3 of titrant.

(c) Calculated values for the analytical concentration of HA and parameters p, r, a, b and c are as follows: $C_{HA} = 1.66 \times 10^{-3}$ M, $p = -0.517$, $r = 6.70 \times 10^{-4}$, $a = -2014$, $b = -10.39$ and $c = 6.89 \times 10^{-3}$.

(d) Calculated values of the equilibrium concentrations and heteroconjugation constant are, [HA] 5.944×10^{-4} M, [BH^+] 3.62×10^{-4} M, [A^-] 2.93×10^{-4} M, [B] 6.33×10^{-6} M, [AHA^-] 6.92×10^{-5} M, [BHB^+] 9.13×10^{-8} M, [AHB] 6.3×10^{-4} M and log $\vec{K}_{AHB} = 5.2_3$.

The log $\vec{K}_{AHB}$ values determined for the corresponding titration points of the two representative systems are given in Fig. 2. The characteristic behaviour around log (C_{HA}/C_B) = 0 is typical of all the systems studied. For systems with negative ΔpK_a^{AN} (*e.g.* 2,4,6-tribromophenol–piperidine), log $\vec{K}_{AHB}$ increases quite significantly as log (C_{HA}/C_B) rises to 0 and decreases as log (C_{HA}/C_B) falls to 0. Quite the opposite deviations are observed in systems with positive ΔpK_a^{AN} *e.g.* pentachlorophenol–piperidine (Fig. 2). The major reason for such behaviour seems to be the fact that the numerators and denominators in the expressions for p and r of eqn. (22) change their signs around the boundaries of the 'critical region'. As a consequence, the existence of other equilibria that have not been taken into account seems to have a remarkable effect on the calculated equilibrium concentrations and finally on the determined heteroconjugation constant. Among these equilibria, the formation of solvent heteroconjugates (*e.g.* AHS or BHS^+) seems to be the most important since the solvent molecules in the solutions studied exist at a very high equilibrium concentration and their proton accepting properties are not without significance. The significance of the formation of solvent heteroconjugates has recently been raised in a previous paper.[9]

In this study we experienced, to an even greater extent, the same general problems in determining heteroconjugation constants as previously.[9] The worst cases for performing calculations involved (a) C_{HA}/C_B ranges for which log (C_{HA}/C_B) is not far from zero (for all the systems studied), (b) negative log (C_{HA}/C_B) values for systems with highly positive ΔpK_a^{AN} and (c) positive log (C_{HA}/C_B) values for systems with highly negative ΔpK_a^{AN}. Unrealistic sets of results are automatically rejected and we decided not to take into account results derived from the least confident log (C_{HA}/C_B) ranges, even if reasonable results were obtained for some points. Having now completed results from two determinations of the heteroconjugation constants [9] we can give the most detailed explanation yet of such a treatment.

When ΔpK_a^{AN} is highly positive, *e.g.* for system 8, the first portions of the added HA (where log (C_{HA}/C_B) is still strongly negative) are almost completely consumed, essentially owing to the proton exchange reaction. Consequently, their equilibrium concentration is extremely low. Under such conditions even an insignificant involvement of solvent molecules in the formation of the heteroconjugates *e.g.* AHS or BHS^+ (not taken into account in the calculations) can make their determination doubtful, as the relevant values may be endowed with great uncertainty. Only a sufficiently high equilibrium concentration of the stronger proton donor (at a significantly positive log (C_{HA}/C_B)) can be determined with satisfactory confidence.

When ΔpK_a^{AN} is highly negative, *e.g.* for system 1, the initial portions of added HA are still essentially involved in interactions with B molecules as these are stronger proton acceptors than acetonitrile. The equilibrium concentration of HA remains sufficiently large since the proton exchange reaction proceeds only to a small degree so it can be determined with confidence. When HA is in excess of B the HA molecules become more strongly involved in the formation of conjugates with the next accessible proton acceptor, which is acetonitrile. Since these conjugates are not taken into account in the calculations, the equilibrium concentration of HA now becomes strongly overestimated. The reasons for problems appearing during calculations involving points not far from log (C_{HA}/C_B) = 0 were explained with full particulars in a previous paper on the same subject.[8] Bearing in mind all the above comments, we decided to choose for our calculations only the regions of greatest confidence: regions of negative log (C_{HA}/C_B) but not too close to zero for systems with negative ΔpK_a^{AN} and regions of positive log (C_{HA}/C_B) but not too close to zero for systems with positive ΔpK_a^{AN}. These rules were strictly applied throughout all the systems studied, although for the equilibrium 6 with pentachlorophenol both regions could be used for the calculations.

The log $\vec{K}_{AHB}$ values for particular substituted phenol–piperidine systems are listed in Table 2 and the relevant dependence between log $\vec{K}_{AHB}$ and ΔpK_a^{AN} is illustrated in Fig. 3. The relationship is fairly linear with slope 0.52. Linearity was to be expected, since in most of the systems studied the access of the key proton to the accepting center of the piperidine molecule is not blocked. Consequently, the heteroconjugation constants are most strongly determined by the ΔpK_a^{AN} value and only slightly affected by steric hindrances created by substituents occupying the 2- and 6-positions of the proton donor molecule.

‡ Note that the value of E_0 is not required for determining equilibrium concentrations and heteroconjugation constants. The method hinges on differences between pK_{HA}, pK_{BH^+} and pH which are reflected by differences between E_{AHA^-}/s, E_{BHB^+}/s and E/s respectively.
§ Average of three independent measurements.

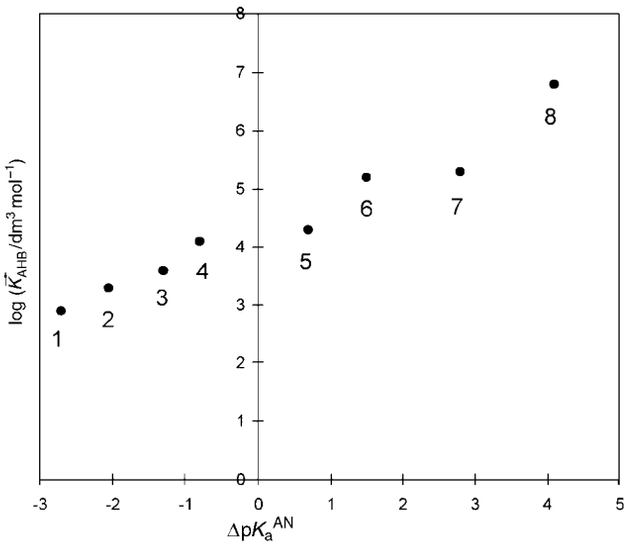

Fig. 3 Experimentally determined log $\vec{K}_{AHB}$ values for particular substituted phenol–piperidine systems as a function of ΔpK_a^{AN}. The slope = 0.52.

An interesting distinction between AHB type and AHA_1^- type heteroconjugates can be made by comparing the quotient Q_{pref} equal to $[K^2_{AHB}/K_{AHA^-}K_{BHB^+}]_{at\ \Delta pK_a=0}$ for phenol–piperidine systems with that of phenol–phenolate systems $[K^2_{AHA_1^-}/K_{AHA^-}K_{A_1HA_1^-}]_{at\ \Delta pK=0}$. The value of such a quotient (if the relative values of homo- and heteroconjugation constants were determined correctly) could express a tendency for the formation of heteroconjugate over both parent homoconjugates. Although the electrometric method does not lead to such a result, one can assume that the degree of overestimation in heteroconjugation constants (though high) is approximately the same (if the same method is used) so the comparison can be made. The corresponding values of log Q_{pref} are *ca.* 4.9 for phenol–piperidine systems and 2.5 for phenol–phenolate systems. The difference is significant as it is on a logarithmic scale and may suggest that in molecular protonic hetero systems, unlike ionic systems, there are some specific conditions advantageous to heteroconjugate formation. Perhaps a simple explanation of this result, based on the fact that AHB type heteroconjugates (in contrast to AHA_1^- heteroconjugates) are wholly neutral, is sufficient. The existence of a total charge in the AHA_1^- type heteroconjugates can render them more sensitive to peripheral interactions, lowering electron density at oxygen or nitrogen atoms involved in hydrogen bond formation, thus contributing to its weakening. Important hydrogen bonds existing in biological systems are formed essentially between neutral molecules. They survive, even though they are theoretically very weak and despite the highly polar aqueous solvent. The relatively easy precipitation of AHB type heteroconjugates from methanol solutions performed in this work in comparison to that of ionic heteroconjugates (no one has ever reported the successful and reproducible preparation of a salt containing a heteroconjugate ion) is strongly indicative of their enhanced stability.

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