# Hydrogen Bonding and Proton Transfer in Hydrido-bis-phenolate Complexes in Acetone

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The homoconjugation,  $(ArO)_2H^-$ , and heteroconjugation,  $Ar'O^- \cdots HOAr$ , (where Ar is aromatic) with proton transfer have been determined in acetone at 298 K. Tetra-alkylammonium phenolates were titrated with a variety of phenols to given homocomplexes and heterocomplexes. Potentiometric data give the overall equilibria constants,  $K_0$ , proton-transfer constants,  $K_{PT}$  and formation constants,  $K_t$ . Two types of heterocomplexes were studied. When  $ArO^-$  is a weaker base than  $Ar'O^-$ , the complexation occurs without proton transfer, as confirmed by the low  $K_0$  values for the reaction. The overall equilibrium constants,  $K_0$ , are large when  $ArO^-$  is a stronger base than  $Ar'O^-$ , as both the equilibrium proton-transfer constant ( $K_{PT}$ ) and equilibrium formation constant ( $K_t$ ) of the hydrogen bond are included in the measurement of  $K_0 = K_t K_{PT}$ .

It has been shown by many authors studying the proton transfer in molecular complexes  $B \cdot HA \Rightarrow BH^+A^-$ 

that symmetrical hydrogen bonding occurs when the difference of  $\Delta p K_a$  (H<sub>2</sub>O) ( $\Delta p K_a$  being the difference between  $p K_a$  values for the acceptor and donor) falls within the range -2 to +7.5. For instance, symmetrical hydrogen bonds in the systems phenol-substituted anilines in cyclohexane, benzoic-acid-substituted pyridines in acetonitrile, and carboxylic acid with base as solvent have been observed at the  $\Delta p K_a$  (H<sub>2</sub>O) values of -1.75, <sup>1</sup> 3.75<sup>2</sup> and 2.3<sup>3</sup> in water, respectively.

The conductiometric, spectrophotometric and potentiometric  $p_aH$  measurements (where  $p_aH$  is the hydrogen-ion activity) in mixtures of phenols with their tetraalkylammonium salts<sup>4, 5</sup> shows stable complex formation of hydrido-bis-phenolate. Formation constants for homo- and hetero-complexes in acetonitrile have been determined.

In conductivity studies some phenols in acetone<sup>6</sup> exhibited a considerable associative ability to form complex anions,  $(ArO)_2H^-$ . In this study the phenols were found to exhibit a stronger interaction in acetone [anion  $(ArO^-)$ -molecule (ArOH)] than carboxylic acids of approximately the same strength in water.

The enthalpy changes for the formation of hydrogen-bonded complexes of the form  $(\text{RCOO})_2\text{H}^-$  and  $(\text{ArO})_2\text{H}^-$  have been determined in propylene carbonate as solvent by a calorimetric method.<sup>7</sup>

The hydrogen-bond energy of homocomplexes decreases almost linearly with decreasing acidity of the proton donor. The ratio of the slopes of the curves for hydrido-bis-carboxylate and hydrido-bis-phenolate is ca. 4.5. This result may mean that substituent effects in aromatic acids are attenuated to a large degree through charge delocalization on hydrogen bonding to the negative phenoxide or benzoate ions.

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Anions with a localized charge can be stabilized in polar aprotic solvents either by homoconjugation:

$$ArO^{-} + HOAr \rightleftharpoons (ArO)_{2}H^{-}$$
 (1)

or by heteroconjugation without proton transfer or, alternatively, with proton transfer

$$ArO^{-} + Ar'OH \rightleftharpoons ArO^{-} \cdots HOAr \text{ or } ArOH^{-} OAr'$$
 (2)

where Ar'OH is a weaker or stronger acid than ArOH.<sup>8,9</sup>

Studies on  $p_aH$  in acetone solution showed that the interaction between phenols (Ar'OH) and phenolates resulted in two distinct types of products. One would be a hydrogen-bonded complex, Ar'OH···-OAr, with the proton still attached to the oxygen of the original Ar'O<sup>-</sup>, whilst for the other, the complex would be formed by proton transfer to the oxygen of ArO<sup>-</sup>, ArOH···-OAr. The hydrogen is transferred to the equilibrium position of proton-transfer anionic bridges, (-OH···-O-)  $\rightleftharpoons$  (-O<sup>-</sup>···HO--), and is determined from a study of the hydrogen-ion activity,  $p_aH$ .

Previous studies<sup>6, 8, 9</sup> were confined to the determination of the formation constants,  $K_{\rm f}$ , of the homo- and hetero-complexes (hydride-bis-carboxylate). In this paper we progress further to the determination of additional equilibrium constants, overall equilibrium constants,  $K_0$ , and the proton-transfer constants,  $K_{\rm PT}$ , and the relationship between formation constants,  $K_{\rm f}$ . We give special attention to proton transfer between anion-proton donors and the interpretation of these data in terms of the acidity scale of non-aqueous solvents.

# **EXPERIMENTAL**

Acetone was purified and rigorously dried.<sup>10</sup> All phenols used (table 1) were recrystallised 2-3 times from methanol or methanol + water mixtures and dried in vacuum over  $P_2O_5$ .

The tetra-n-alkylammonium salts of the substituted phenols were prepared by potentiometric titration of a weighed sample of the phenol with a methanolic solution of the corresponding tetra-alkylammonium hydroxide. After evaporation of the solvent under reduced pressure the salts were recrystallised from ethyl acetate and dried in a vacuum over  $P_2O_5$ . Their purity was checked potentiometric titration with 0.1 mol dm<sup>-3</sup> perchloric acid in glacial acetic acid. All results fell in the range 99.5-100.5%.

Electromotive-force measurements were made with a PHM-52 digital pH meter (Radiometer, Copenhagen) using an S-60 glass electrode (Gliwice, Poland). The reference half-cell was a saturated calomel electrode with a double junction, and the salt bridge was filled with a  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> acetone solution of tetra-n-butylammonium perchlorate. The electrode was checked every day in picric-acid-picrate buffers. All measurements were carried out at  $298 \pm 0.1$  K.

#### RESULTS

# CALIBRATION OF THE GLASS ELECTRODE

The reversibility of the glass electrode was checked by e.m.f. measurements in buffer solutions containing  $C_{Bu_4NPi} = 4 \times 10^{-3}$  mol dm<sup>-3</sup> + picric acid,  $C_{HPi} = 1 \times 10^{-1}$  mol dm<sup>-3</sup>. The p<sub>a</sub>H values of these solutions were calculated, assuming complete dissociation of Bu<sub>4</sub>NPi in dilute solution,<sup>11</sup> and

$$pK_{HPi}^{acetone} = 6.3^{12} p_a H_{ref} = pK_{HPi} + \log f_{\frac{1}{2}}$$

where the subscript  $\frac{1}{2}$  stands for  $C_{\text{HPi}} = C_{\text{salt}}$ . The activity coefficient was calculated from the expression  $-\log f = 3.76 \sqrt{I}$ .

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Table 1.—Hetero- and homo-conjugation of phenolates (ArO<sup>-</sup>) with substituted phenols (ArOH), overall equilibrium constants ( $K_0$ ), formation constants ( $K_f$ ) and proton-transfer constants ( $K_{PT}$ ) in acetone at 298 K

quaternary salt, R <sub>4</sub> N <sup>+</sup> ArO <sup>-</sup>	log K <sub>PT</sub> calcd [eqn (8)]	$\log K_0^b$ calcd [eqn (7)]	log K <sub>f</sub> calcd [eqn (9)]
heterocomplexes, (Ar	r'OHOAr) <sup>-</sup>		
I.),N 2.4-dinitrophenolate	-7.0	$3.04 \pm 0.08$	3.04
I.),N 2.4-dinitrophenolate	-6.6	$2.95 \pm 0.07$	2.95
I, N 2, 4-dinitrophenolate	- 5.4	$2.98 \pm 0.07$	2.98
f,),N pentachlorophenolate	4.4	$3.27 \pm 0.08$	3.27
[,) N pentachlorophenolate	-4.0	$3.52 \pm 0.08$	3.52
[,) N 2,5-dinitrophenolate	-3.5	$3.23 \pm 0.06$	3.23
(a) N 2,5-dinitrophenolate	-2.9	$3.78 \pm 0.09$	3.78
<sup>5</sup> ) <sup>4</sup> N pentachlorophenolate	- 2.8	$3.71 \pm 0.08$	3.71
) N 2,4-dinitrophenolate	-2.6	$3.42\pm0.07$	3.42
) <sup>A</sup> N 2,5-dinitrophenolate	-1.3	$3.79 \pm 0.09$	3.79
N 2,4,6-trichlorophenolate	+0.2	$3.58 \pm 0.06$	3.38
"N 2,6-dichlorophenolate	+1.2	$4.33\pm0.10$	3.13
, N 2,4,6-trichlorophenolate	+1.4	$4.70 \pm 0.12$	3.30
") <sup>4</sup> N 2,5-dinitrophenolate	+1.5	$4.30 \pm 0.10$	2.80
() N 2,6-dichlorophenolate	+ 2.8	$4.85 \pm 0.11$	2.05
<sup>1</sup> N 2,4,6-trichlorophenolate	+4.2	$5.42 \pm 0.14$	1.22
) <sub>4</sub> N 2,6-dichlorophenolate	+5.6	$6.25 \pm 0.12$	0.65
homocomplexes, Ar	roHOAr <sup>-</sup>		
<sup>1</sup> ,N 2,4-dinitrophenolate	0	$3.41 \pm 0.07$	3.41
<sub>5</sub> ) <sub>4</sub> N pentachlorophenolate	0	$4.28 \pm 0.09$	4.28
") <sub>4</sub> N 2,5-dinitrophenolate	0	$4.59 \pm 0.10$	4.59
) <sup>4</sup> N 2,4,6-tribromophenolate	0	$4.32 \pm 0.12$	4.32
N <sub>4</sub> N 2-nitrophenolate	0	$4.12 \pm 0.09$	4.12
<sub>9</sub> ) <sub>4</sub> N 2,4,6-trichlorophenolate	0	$4.20 \pm 0.09$	4.20
) <sub>4</sub> N 3,5-dichlorophenolate	0	$4.02 \pm 0.12$	4.02
) <sub>4</sub> N 2,6-dichlorophenolate	0	$3.50 \pm 0.10$	3.50

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The glass electrode was calibrated every day in a picrate buffer. For our electrode13

$$p_a H = (E'_0 - E)/W = (765 - E)/42.5$$

where W is the Nernst slope, and  $E'_0$  and E are the apparent potential of the reference electrode and the measured potential, respectively.

# DETERMINATION OF THE PROTON-TRANSFER CONSTANTS, $K_{PT}$ , THE FORMATION CONSTANTS, $K_f$ , AND THE OVERALL EQUILIBRIUM CONSTANTS, $K_0$

The reaction between the proton donor Ar'OH and proton acceptor  $ArO^-$  in an aprotic solvent may lead to the formation of hydrogen-bonded complexes with proton transfer (PT) or without proton transfer.

A general scheme for the formation of the heterocomplexes can be written as follows:  $\kappa$ 

$$ArO^{-} + Ar'OH \rightleftharpoons^{R_{PT}} ArOH + Ar'O^{-}$$
 (3)

$$Ar'O^{-} + HOAr \rightleftharpoons^{K_t} Ar'O^{-} \cdots HOAr$$
(4)

$$ArO^{-} + Ar'OH \rightleftharpoons^{K_0} Ar'O^{-} \cdots HOAr$$
(5)

where  $K_0$ ,  $K_{PT}$  and  $K_f$  are the equilibrium constants of the overall reaction, the proton-transfer constant and the formation constant, respectively.

The overall equilibrium constant  $K_0$  is related to  $K_{PT}$  and  $K_f$  by

$$K_0 = K_{\rm PT} K_{\rm f} \tag{6}$$

and was calculated from the potentiometric data using eqn (7) adapted by us<sup>14</sup> from the study by Kolthoff and Chantooni:<sup>4</sup>

$$K_0 = C_{\rm R_4N^+ArO^-} r^2 - r(C_{\rm Ar'OH} + C_{\rm R_4N^+ArO^-}) + C_{\rm Ar'OH} / r(C_{\rm R_4N^+ArO^-} - C_{\rm Ar'OH})$$
(7)

where  $r = a_{\rm H} f/a_{\frac{1}{2}} f_{\frac{1}{2}}$  and  $a_{\frac{1}{2}}$  and  $f_{\frac{1}{2}}$  are values at midpoint  $(C_{\rm R_4N^+ArO^-} = C_{\rm ArOH})$ . Plots of  $p_{\rm a}H$  against log  $C_{\rm Ar'OH}/C_{\rm R_4N^+ArO^-}$  of mixtures of phenols with different

quaternary ammonium salts are presented in fig. 1(a) and (b).

If we express the ionization constant,  $K_a$ , of an acid ArOH in acetone medium (S) by

$$ArOH + S \rightleftharpoons SH^{+} + ArO^{-}$$
$$K_{a} = [SH^{+}][ArO^{-}] f_{SH} + f_{ArO^{-}}/[S][ArOH] f_{S} f_{ArOH}.$$

We assume 
$$f_{ArOH}$$
 and  $f_{S}$  to be equal to 1 at low concentrations and

$$f_{\rm SH^+} = f_{\rm ArO^-} = f_{\pm}.$$

By replacing  $[SH^+] f_{SH^+}$ ,  $[ArO^-]$  and [ArOH] by  $a_{H^+}$ ,  $C_{R_4N^+ArO^-}$  and  $C_{ArOH}$ , respectively, and taking logarithms we obtain

$$pK_{a}^{AC} = p_{a}H - \log(C_{R_{4}N^{+}ArO^{-}}/C_{ArOH}) - \log f_{\pm}.$$

For a medium point (subscript  $\frac{1}{2}$ , at  $C_{R_4N^+ArO^-} = C_{ArOH}$ ) the equation may be written as follows<sup>13, 14</sup>

$$\mathsf{p}K_{\mathrm{a}}^{\mathrm{AC}} = \mathsf{p}_{\mathrm{a}}\mathsf{H}_{\frac{1}{2}} - \log f_{\frac{1}{2}}.$$

This equation is correct for the homosystems  $R_4N^+ArO^- + ArOH$ .



FIG. 1.—Relationship between log  $C_{\rm Ar'OH}/C_{\rm R_{4}N^{+}ArO^{-}}$  and  $p_{\rm a}H$  in acetone at 298 K. Numbers identify the systems listed in table 1.

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FIG. 2.—Relationship between  $p_aH_i(C_{phenol} = C_{quaternary salt})$  in homocomplexes and heterocomplexes in acetone at 298 K plotted against  $\Delta pK_a^{AC}$ , where

$$\Delta p K_{a}^{AC} = p K_{a(acceptor)}^{AC} - p K_{a(donor)}^{AC}.$$

Numbers identify the systems listed in table 1.

Hence, we consider the reaction of an acid, Ar'OH, which involves the following reaction  $ArO^- + Ar'OH \rightleftharpoons ArOH + Ar'O^-$ 

for which the equilibrium constant,  $K_{\rm PT}$  is

$$K_{\rm PT} = K_{\rm a(Ar'OH)}^{\rm AC} / K_{\rm a(ArOH)}^{\rm AC}.$$
(8)

Hence the values of  $K_{\rm f}$ , the equilibrium constants for the formation of hydrogen bonding of heterocomplexes with proton transfer, may be found, since

$$\log K_{\rm f} = \log K_0 - \log K_{\rm PT}.\tag{9}$$

In the case when  $K_{\rm PT}$  is close to, or less than, unity, the value of the overall equilibrium constant,  $K_0$ , is equal to that of the formation constant,  $K_0 = K_{\rm f}$ . For instance, this case if found in systems where  $pK_{\rm a(Ar'OH)}^{\rm AC} > pK_{\rm a(ArOH)}^{\rm AC}$ , table 1.

In mixtures of  $R_4N^+ArO^-$  with a non-conjugated phenol Ar'OH in acetone, where the proton transfer is not complete, the  $p_aH$  change is relatively small, but the decrease in  $p_aH$  is sharp where the proton transfer is complete, fig. 1(*a*).

For systems in which the proton is attached to the proton-donor group Ar'OH  $(\Delta p K_a^{AC} < 0)$ , the plot of the function

$$p_a H = f(\log C_{Ar'OH}/C_{ArO})$$

is linear.

In heterosystems in which proton transfer occurs ( $\Delta p K_a^{AC} > 0$ ) the plot of the function  $p_a H = f(\log C_{Ar'OH}/C_{ArO^-})$ 

is non-linear, and the curve has a sigmoidal shape. The plots of 
$$p_aH$$
 of a mixture of



FIG. 3.—Formation constants, log  $K_t$ , of homocomplexes,  $(ArO)_2H^-$ , in acetone at 298 K plotted against  $pK_{a(ArOH)}^{AC}$ . Numbers identify the systems listed in table 1.

an acid and salt without proton transfer,  $pK_{a(acceptor)}^{AC} < pK_{a(donor)}^{AC}$  are linear in fig. 1(a) and (b), curves 1-10.

Some heterosystems in which  $pK_{a(acceptor)}^{AC} > pK_{a(donor)}^{AC}$  [fig. 1(*a*) and (*b*), curves 13-17] are indicative of the proton-transfer reaction, *e.g.* curve 17, where  $\Delta pK_a^{AC} = 5.6$ :

$$C_6Cl_5OH + Cl_2C_6H_3O^- \rightarrow C_6Cl_5O^- \cdots HOC_6H_3Cl_2$$

Consequently, the  $p_aH$  greatly decreases, and the plot assumes a sigmoidal shape. Calculated values of  $K_{PT}$ ,  $K_0$  and  $K_f$  obtained from the plots of fig. 1(a) and (b) are given in table 1 for each system.

Plots of  $p_a H_1$  at the point  $(C_{R_4N^+ArO^-} = C_{Ar'OH})$  in the systems studied as a function  $\Delta p K_a^{AC}$ , where

$$\Delta p K_{a}^{AC} = p K_{a(acceptor)}^{AC} - p K_{a(donor)}^{AC}$$

of mixtures of these phenols with different tetra-alkylammonium salts are presented in fig. 2, and exhibit a pronounced maximum around  $\Delta p K_a^{AC} = 0$ .

Let us consider the two systems: (1) without proton transfer  $[3,5-Cl_2ArOH +2,5(NO_2)_2ArO^-$ ,  $\Delta pK_a^{AC} = -2.90]$  and (2) with proton transfer  $[2,4,6-Br_3ArOH +2,6-Cl_2ArO^-$ ,  $\Delta pK_a^{AC} = +2.80]$ . The observed  $p_aH$  values are comparable,  $22 \pm 0.2$ . From the  $p_aH_1$  values (at the point  $C_{R_4N^+ArO^-} = C_{Ar'OH}$ ) as a function of  $\Delta pK_a^{AC}$ , fig. 2, the proton concentration has a minimum at  $\Delta pK_a^{AC} = 0$ , as a result of the formation of homoconjugate  $(ArO)_2H^-$  ions.

In fig. 3 the stability constants of the homocomplexes,  $\log K_{(ArO)_2H^-}$ , are plotted against  $pK_{a(ArOH)}^{AC}$  on the acetone scale. The largest increase in stability is observed in the region of 20  $pK_a^{AC}$  units. In acetone, the  $K_f$  values of homocomplexes of substituted phenols are of the order of 10<sup>4</sup> or less. In the series considered in fig. 3, the stability of the homocomplexes increases with  $pK_a^{AC}$  up to  $pK_a \approx 20$ , and then drops with the  $pK_a^{AC}$  of phenols.

As can be seen in fig. 4, the plot of the overall equilibrium constant,  $\log K_0$  against  $\Delta p K_a^{AC}$ , is linear over the  $\Delta p K_a^{AC}$  range from -7 to 0. Above the latter value,  $\log K_0$  markedly increases.

Linear plots of log  $K_{ArOHOAr}^{f}$  against  $\Delta p K_{a}^{AC}$  were obtained for heterocomplexes. An increase in the formation constant,  $K_{f}$ , in acetone was found with decreasing  $\Delta p K_{a}^{AC}$ , whereas for  $\Delta p K_{a}^{AC} > 0$  the stability decreased more markedly.

Systems characterised by  $pK_{a(donor)}^{AC}(Ar'OH) > pK_{a(acceptor)}^{AC}(ArOH)$  are represented

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FIG. 4.—Plots of overall equilibrium constants,  $\log K_0$ , and formation constants,  $\log K_t$ , for homocomplexes ( $\bigcirc$ ) and heterocomplexes ( $\bigcirc$ ) in acetone, at 298 K, as a function  $\Delta p K_a^{AC}$  on the acetone scale. Numbers identify the systems listed in table 1.

by entries 1-10 in table 1 and in fig. 4. For these  $\Delta p K_a^{AC}$  is negative. As shown in fig. 4 the overall constants,  $K_0$ , of the reaction are low under these conditions, as proton transfer does not take place. The intermediate region, where  $\Delta p K_a^{AC} = 0$ , corresponds to the formation of homocomplexes,  $(ArO)_2H^-$ , with log  $K_0$  ranging from 3.41 to 4.59.

The largest change of overall equilibria occurs in the region where  $\Delta p K_a^{AC} > 0$ . In this case, the proton is transferred from the less basic donor Ar'OH to the more basic acceptor ArO<sup>-</sup>. The overall constant  $K_0$  does not represent equilibria for the formation of the hydrogen bond alone  $(K_f)$ , but also includes that of the proton transfer  $(K_{PT})$ . The overall equilibrium constant,  $K_0$ , is related to  $K_{PT}$  and  $K_f$  by

$$\log K_0 = \log K_{\rm PT} + \log K_{\rm f}.$$

This difference is illustrated by comparison of systems 8 and 15.

The values for system 15 are

$$2,6-Cl_2C_6H_3O^- + 2,4,6-Br_3C_6H_2OH \rightarrow (2,6-Cl_2C_6H_3OH \cdots OC_6H_2Br_3-2,4)^-$$

where log  $K_0 = 4.85$  and  $\Delta p K_a^{AC} = 2.80$ , while for system 8 one has

$$C_6Cl_5O^- + 2,4,6$$
- $Br_3C_6H_2OH \rightarrow (C_6Cl_5O^- HOC_6H_2Br_3-2,4,6)^-$ 

where  $\log K_0 = 3.71$  and  $\Delta p K_a^{AC} = -2.80$ .

Similar results were obtained for other systems with  $\pm \Delta p K_a^{AC}$ , namely systems 3, 17 and 5, 16: *viz*.

(3) 2,4,6-tribromophenol+2,4-dinitrophenolate, log  $K_0 = 2.98$ 

(17) pentachlorophenol+2,6-dinitrophenolate, log  $K_0 = 6.25$ 

(5) 2-nitrophenol + pentachlorophenolate,  $\log K_0 = 3.52$ 

(16) pentachlorophenol + 2,4,6-trinitrophenolate,  $\log K_0 = 5.42$ 

# CONCLUSIONS

The main interaction in our study of phenolate-phenol by hydrogen bonding shows stable homocomplexes with  $K_{\rm f} \simeq 10^4$  and heterocomplexes with  $K_{\rm f} \approx 10^2$ -10<sup>3</sup>.

The most important implication of this work is that contained in fig. 4, showing  $K_0$ ,  $K_f$  and  $\Delta p K_a^{solvent}$  to have a complex relationship. When  $\Delta p K$  is negative or zero, then log  $K_0 = \log K_f$ . Formation values  $K_f$  at whole range  $(-\Delta p K_a)$  are not changed as much. However, when  $\Delta p K$  is positive for the systems, then log  $K_0$  diverges rapidly from  $K_f$ . Complexes formed after proton transfer at  $\Delta p K_a^{AN}$  in the positive range undergo a change information constant more markedly.

In future, simple statements concerning  $\Delta p K_a^{solvent}$  and log  $K_0$  for proton transfer should either not be made or should carry the qualification that  $\Delta p K_a$  is negative or zero. When  $\Delta p K_a^{solvent}$  is positive, then both  $K_0$  and  $K_f$  must be given.

Further, it is clear that the  $\Delta p K_a$  scale used must be that for the relevant solvent. Whereas comparisons made in the past have used the water scale for  $\Delta p K_a$ , maxima in the measured quantities, *e.g.* in the proton chemical shift, have been taken as showing symmetrical hydrogen-bond formation between acid and base at  $\Delta p K_a^{H_2O}$ values ranging between -2 and +7.5. It is self-evident that symmetry of hydrogen-bond formation will occur for equal basicity/acidity of the two components, at  $\Delta p K_a^{solvent} = 0$ . This has been demonstrated in another paper<sup>5</sup> for phenolate complexes in acetonitrile when  $\Delta p K_a^{AC}$  was used.

Therefore, we urge that  $K_0$ ,  $K_f$  and  $\Delta p K_a^{solvent}$  for proton transfer systems should be interpreted in a more meaningful manner and that  $\Delta p K_a^{solvent}$  values used should be those for the relevant solvent. It should no longer be acceptable to use  $\Delta p K_a^{H_2O}$ values when discussing proton-transfer equilibria in non-aqueous systems.

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