Electrophoretic detection and evaluation of heteroconjugate anion formation between Brønsted acids and the perchlorate ion in acetonitrile

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Capillary electrophoresis is effective in the detection and evaluation of weak interactions in solution, and verifies the heteroconjugation of Brønsted acids (phenols and carboxylic acids) with the perchlorate ion in acetonitrile, a relatively high permittivity medium.

Both heteroconjugation and homoconjugation play important roles in acid–base equilibria in aprotic solvents.[1,2] Kolthoff and Chantooni[3] studied heteroconjugate anion formation between phenols and chloride ions in acetonitrile (AN) by conductometry and more recently Zundel and co-workers have reported heteroconjugate formation between various Brønsted acids and trialkylamine *N*-oxide in AN by IR spectroscopy.[4–6] However, these methods can detect heteroconjugation, only when the equilibrium constants are large enough. Here we report the effective detection and evaluation of much weaker heteroconjugate formation between the perchlorate ion and phenols or carboxylic acids in AN. For this purpose, capillary electrophoresis proved very effective.

Fig. 1 shows examples of electropherograms of selected phenols in AN containing tetraethylammonium perchlorate as a running electrolyte. Since the phenols were detected at the negative end, the retardation of phenols from acetone added as an electroosmotic flow marker indicated that phenols form anionic species. The behaviour of anionic phenols becomes marked with increasing salt concentration or increasing the hydrogen bond acceptor ability of the anions added (from ClO_4 towards *e.g.* Cl^-). Similar results were obtained with carboxylic acids. The p*K*a values of the Brønsted acids tested range from 11.0 (picric acid) to 27.2 (phenol) and that of $HClO_4$ is 1.57 in AN,[2] suggesting that complete proton transfer from an acid to perchlorate does not take place. These results strongly indicate that phenols and carboxylic acids form heteroconjugate anions with perchlorate.

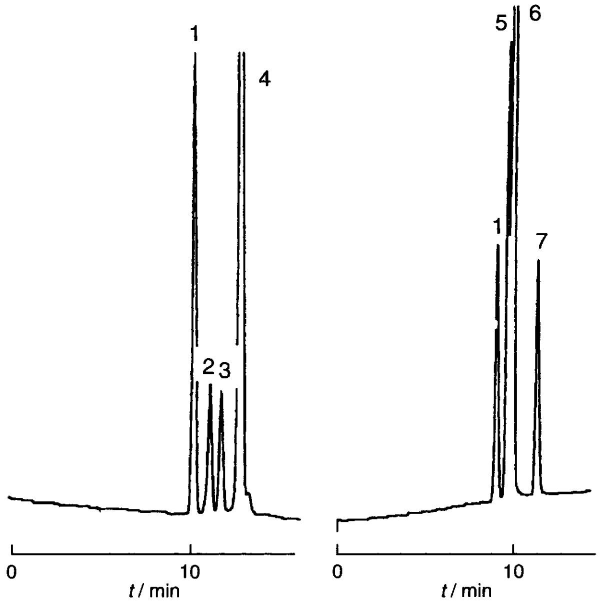

Fig. 1 Electropherograms of selected phenols with 85 mmol dm^{-3} tetraethylammonium perchlorate AN. Capillary, 50 μm i.d. × 375 μm o.d., 57.8 cm long. Applied voltage, 15 kV. Detection at 265 nm. Peak identification: 1 = acetone (electroosmotic flow marker); 2 = p-*tert*-butylphenol; 3 = phenol; 4 = resorcinol; 5 = 2,4-dinitrophenol; 6 = picric acid and 7 = *p*-nitrophenol.

The electrophoretic behaviour of the Brønsted acids were analysed on the basis of 1 : 1 heteroconjugate anion formation, eqns. (1), (2), where *v* and *t* denote electrophoretic velocity

$$v_s = v_{app} - v_{eo} = L(1/t_{app}{}^{-1}/t_{eo}) = \alpha\, v_{hetero} \qquad (1)$$

$$1/(1/t_m{}^{-1}/t_{eo}) = [1/(K_{HAX}\, C) + 1]L\ F/(E\ \lambda_{hetero}) \qquad (2)$$

and the migration time, subscripts s, app, eo and hetero refer to solute, apparent, electroosmotic and a heteroconjugate anion, α = the degree of heteroconjugate anion formation, K_{HAX} = heteroconjugate anion formation constant, C = the perchlorate ion concentration, L = the effective length of a capillary (36.8 cm in the present work), E = the electric field strength (15 kV applied to the entire capillary, 57.8 cm), F = Faraday constant and λ_{hetero} = the molar ionic conductivity of a heteroconjugate anion. The last term was corrected according to the Onsagar equation.[7]

If K_{HAX}, λ_{hetero}, and *a* in the Onsagar equation are taken as adjustable parameters, the best fit was given by a set of unrealistic parameters partly because of data scatter due to very small formation constants. Our measurements for the heteroconjugation of phenols with Cl and NO_3 gave λ_{hetero} = 68.3 S cm^2 mol^{-1} in AN. The molar ionic conductivity values at infinite dilution in AN are almost identical for Cl (98.7 S cm^2 mol^{-1}) and ClO_4 (103.7 S cm^2 mol^{-1}). A value of λ_{hetero} = 68.3 S cm^2 mol^{-1} is reasonable with reference to λ_{hetero} = 55 S cm^2 mol^{-1} for *p*-bromophenol–Cl heteroconjugate anion previously reported.[3] Assuming a = 5 Å, we calculated K_{HAX} values, Table 1, together with pK_a values in water;[8,9] although comparison with pK_a values in AN is essential, available data are very few. We attempted to determine K_{HAX} for benzoic acids other than those listed in Table 1, but could not because of their very small apparent mobility due to very small K_{HAX} values. We therefore focussed our discussion on the data for phenol heteroconjugation.

As known for heteroconjugate ion formation in the gaseous phase,[10,11] there is a close relationship between the acidity of Brønsted acids and heteroconjugate ion formation. A linear relationship is found between pK_a values in water and heteroconjugate ion formation constants for *p*- and *m*-substituted phenols, eqn. (3).

$$\log K_{HAX} = 1.14\text{–}0.159\ pK_a\ (r = 0.922) \qquad (3)$$

However, as indicated already,[11] there is a much closer relationship between log K_{HAX} of *p*- and *m*-substituted phenols and the pK_a values of *p*- and *m*-substituted benzoic acids, eqn. (4).

$$\log K_{HAX} = 1.88\text{–}0.55\ pK_a\ (r = 0.969) \qquad (4)$$

These results imply that the acidity of phenols is predominantly determined by resonance effects, which are not important in heteroconjugate ion formation. Heteroconjugate ion formation depends much on the electron density of the oxygen atom in the hydroxy group of *p*- and *m*-substituted phenols. Thus, log K_{HAX} for *p*- and *m*-substituted phenols linearly changes with the pK_a of *p*- and *m*-substituted carboxylic acids rather than with that of *p*- or *m*-substituted phenols.

Table 1 Formation constants (K_{HAX} of heteroconjugate anions of phenols and carboxylic acids with the perchlorate ion

Compound	K_{HAX}[a]	σ	pK_a[b]
Phenol			
phenol	0.44	0.02	9.99
o-methyl-	0.34	0.01	10.26
m-methyl-	0.34	0.01	10.00
p-methyl-	0.34	0.01	10.26
p-ethyl-	0.32	0.02	10.0
p-isopropyl-	0.24	0.02	
p-*tert*-butyl	0.25	0.01	10.25[d]
o-nitro-	—[c]	—	7.22
p-nitro-	0.95	0.10	7.15
p-chloro-	0.54	0.03	9.43
p-amino-	—	—	10.30
2,4-dinitro-	0.24	0.01	4.08
2,4,6-trinitro-	0.32	0.01	0.42
1-naphth	0.32	0.05	9.30
resorcinol	0.79	0.05	9.30
Benzoic acid			
benzoic acid	0.25	0.01	4.204
o-methyl-	0.22	0.02	3.90
p-methyl-	0.18	0.01	4.362
o-nitro-	0.30	0.01	2.18
p-nitro-	0.38	0.01	3.441
phthalic acid	0.28	0.03	2.950

[a] Determined according to eqn. (1) with 20–85 mmol dm^{-3} tetraethylammonium perchlorate solution (n = 7). [b] pK_a values in water from ref. 8. [c] Not determined. [d] From ref. 9. Amino-, *p*-ethyl, *p*-propyl- and *tert*-butyl-benzoic acids did not give any resolved peaks.

For *o*-substituted phenols, a very different tendency can be seen. When the *o*-substituents are small (*e.g.* methyl), its heteroconjugate formation constant falls on the log K_{HAX}–pK_a plot for *m*- and *p*-substituted phenols. However, when the *o*-substituent is large and electron-withdrawing (*e.g.* a nitro group), the ability to form heteroconjugate anions is much decreased. This phenomenon has also been observed for homoconjugate anion formation of phenols.[2,12]

Footnote

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