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Protonation of Anion Radicals in Polar Aprotic Solvents. A Search for Microscopic Rate Constants

Merete Folmer Nielsen

Anion radicals derived from aromatic hydrocarbons have been used as electrogenerated bases for the study of proton transfer reactions in polar aprotic solvents. The main objective has been to quantify the multiple equilibria - especially hydrogen-bonding equilibria - involving the proton source in polar aprotic solvents, in order to arrive at the "true" microscopic rate constants for the proton transfer, by correcting the observed rates for the influence of these equilibria.

The general reaction scheme for the over-all formation of the dihydrogenated product (AH_2) from the aromatic hydrocarbon (A) and the proton donor (HB) is given by reactions (1)-(4), where (2) is the rate determining step [1-3].

$$A + e^- \rightleftharpoons A^- \quad (1)$$

$$A^- + HB \xrightarrow{k_2} AH^\cdot + B^- \quad (2)$$

$$AH^\cdot + A^- \xrightarrow{fast} AH^- + A \quad (3)$$

$$AH^- + HB \xrightarrow{fast} AH_2 + B^- \quad (4)$$

The anion radicals are formed by electrochemical reduction of the parent hydrocarbon, and the rate of reaction k_{obs} of the initially formed anion radical is followed by voltammetric techniques [3,4].

The rate law associated with the reaction scheme (1)-(4), assuming steady state for $AH^\cdot$ and AH^-, is given by eqn. (5).

$$-\frac{d[A^-]}{dt} = 2k_2[A^-][HB] \quad (5)$$

The main question is, how a measured rate of reaction of A^-, k_{obs}, is interpreted in terms of the rate constant for the microscopic step (2), k_2, taking into account that the acid (phenols, benzoic acid or formal carbon acids as dimedone, acetyl acetone and ethyl acetoacetate) may participate in the following parallel equilibria (here an in the following "/" denotes a hydrogen-bond), when the reactions are carried out in a polar aprotic solvent (DMSO, DMF, PC and MeCN have been used).

$$HB + B^- \overset{K_6}{\rightleftharpoons} HB/B^- \quad (6)$$

$$HB + HB/B^- \overset{K_7}{\rightleftharpoons} HB/HB/B^- \quad (7)$$

(6) and (7): homoconjugation

$$2\,HB \overset{K_8}{\rightleftharpoons} HB/HB \quad (8)$$

dimerization

$$HB \overset{K_9}{\rightleftharpoons} BH \quad (9)$$

tautomerization

$$HB + solv \overset{K_{10}}{\rightleftharpoons} HB/solv \quad (10)$$

hydrogen-bonding to the solvent

In the following the effect of simple homoconjugation, eqn. (6) [3,5-7], keto-enol tautomerization, eqn. (9) [8-9], and hydrogen-bonding to the solvent, eqn. (10) [10], will be discussed.

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The effect of the homoconjugation equilibrium, eqn. (6)

It is well known that the polar aprotic solvents applied in these studies, DMSO, DMF, PC and MeCN, are inefficient in solvating anions [11], and the anions produced during the proton transfer reaction, B^-, are therefore to a large extent stabilized by hydrogen-bonds from the neutral acid. When HB = phenol the equilibrium constant, K_6, is known in DMSO, $K_6 = 2.3 \times 10^3\ M^{-1}$ [12].

The large value of K_6 results in a change in the over-all stoichiometry of the protonation reaction. Mechanism (1)-(4) has the over-all stoichiometry in eqn. (11), while the inclusion of equilibrium (6) changes the over-all stoichiometry to eqn. (12).

$$2\ A^- + 2\ HB \longrightarrow AH_2 + A + 2\ B^- \qquad (11)$$

$$2\ A^- + 4\ HB \longrightarrow AH_2 + A + 2\ HB/B^- \qquad (12)$$

When the acid is present in a large excess, the change in stoichiometry has no influence on the measured rate of reaction, but when $C^\circ_{HB}/C^\circ_A < 10$, the change in stoichiometry must be taken into account [3,5]. Measurements carried out at $C^\circ_{HB}/C^\circ_A = 1$ (A = anthracene, HB = phenol, solvent = DMSO) showed, *Fig. 1*, that reaction (6) behaves as a fast equilibrium with the equilibrium constant reported in ref. 12 and that the rate constant, k_2(DMSO), determined from the working curve in *Fig. 1*, $(2.6 \pm 0.2) \times 10^3\ M^{-1}s^{-1}$, is identical within experimental error to the value of k_2(DMSO) obtained with phenol in a large excess, i.e. with no indication of the homoconjugation complex as an active proton donor. This result was confirmed by application of the salt PhOH/PhO^-,Bu_4N^+ as the proton source; in this case the concentration of "free" PhOH is so small (due to the large value of K_6) that possible contributions from PhOH/PhO^- as the active proton donor is likely to be of importance. However, as shown in *Fig. 2*, the experimental data fit the working curve corresponding to the mechanism where only PhOH is an active proton donor, and the rate constant calculated from the fit is equal to $(2.34 \pm 0.16) \times 10^3\ M^{-1}s^{-1}$, i.e. in good agreement with the values cited above [7].

The experiments were taken as evidence for a two-step mechanism in which PhOH has to dissociate from the homoconjugation complex *before* the proton can be transferred.

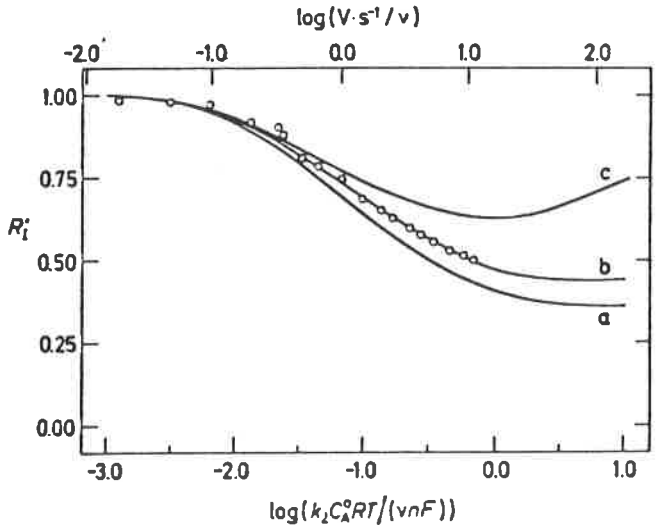

FIGURE 1. - *Derivative cyclic voltammetry working curves for (a) mechanism (1)-(4); (b) mechanism (1)-(4), (6) assuming reaction (6) to be fast and reversible with* $K_6 C^\circ_A = 2.3$; *(c) mechanism (1)-(4), (6) assuming reaction (6) to be fast and irreversible. In all cases* $C^\circ_{HB}/C^\circ_A = 1$. *The experimental points (circles) are for* $C^\circ_{PhOH} = C^\circ_{AN} = 1$ *mM obtained at the sweep rates indicated by the top scale of the figure.* T = 20.4 °C. *(Reproduced from ref. [7]).*

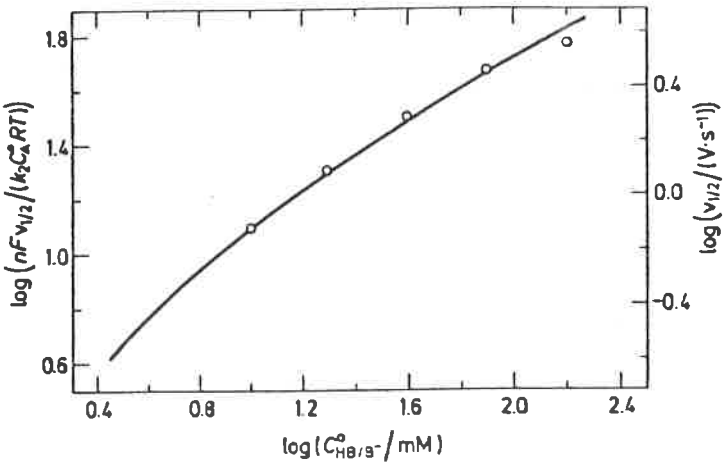

FIGURE 2. - *Derivative cyclic voltammetry working curve for mechanism (1)-(4), (6) using HB/B⁻ as the proton source and assuming reaction (6) to be fast and reversible with* $K_6 C^\circ_A = 2.3$. *The experimental points (circles) are for* $C_{AN} = 1$ *mM obtained at the sweep rates indicated on the right-hand scale.* T = 20.7 °C. *(Reproduced from ref. [7]).*

The effect of the keto-enol tautomerization equilibrium, eqn. (9)

The influence of equilibrium (9) is much more serious from a mechanistic point of view than the homoconjugation equilibrium discussed above. Acids like dimedone (DIMH), acetyl acetone (AAH) and ethyl acetoacetate (EAAH) exist as a mixture of the keto form (C-acid) and the enol form (O-acid) in most solvents, and the participation of both tautomers as active proton donors can be envisaged.

The equilibrium constants for the tautomerization, K_9, for the three acids in DMSO, DMF and MeCN as determined by NMR, can be found in *Table I* [9]. The most notable observation is the change in K_9 for dimedone when the solvent is changed from DMSO or DMF to MeCN. This observation reflects the fact that contrary to acetyl acetone and ethyl acetoacetate, dimedone is not able to stabilize the enol form by formation of an *intra*-molecular hydrogen-bond.

Consequently, hydrogen-bond stabilization of the enol form of

TABLE I. - *Equilibrium constants,* K_9, *for the keto-enol equilibrium of the applied carbon acids determined by NMR at 20 °C. Values in parentheses are literature values.*

	Solvent					
Acid	DMSO		DMF		MeCN	
DIMH	> 100	(> 20) (> 21) (94)	> 100	(85) (13)	1.9	(2.3)
AAH	1.4	(1.95) (1.6) (1.6)	1.9		1.3	(1.6) (1.2)
EAAH	0.02	(0.05) (0.023)	0.04		0.04	(0.052)

dimedone can only be achieved by hydrogen-bonding to the solvent ; therefore the value of K_9 for dimedone changes when going from DMSO or DMF (strong hydrogen-bond acceptors) to MeCN (weak hydrogen-bond acceptor).

The apparent thermodynamic acidity constants are known for the three acids in DMSO [13], and from these values and the corresponding K_9-values the thermodynamic acidities of the individual tautomers can be calculated, *Table II*.

In all cases the tautomer present in the smallest amount will be the thermodynamically most acidic. Kinetically, the enol forms are in general expected to be more acidic than the keto form (O-acids versus C-acids) even when the thermodynamic acidities are opposite.

The NMR-measurements showed that in the absence of any catalyst, the keto-enol interconversion is a slow process. However, during the proton transfer reaction enolate anions are formed, and as most bases they catalyze the interconversion, i.e. the reaction is autocatalytic. Approximate rate constants for the base catalyzed interconversion were determined by NMR, and by simulations based on these rate constants and on the assumption that the enol form is the only active proton donor, it was shown that the three systems, under the conditions of the voltammetric experiments, with only a few exceptions could be regarded as true equilibrium systems.

For all three acids the experimental data were in agreement with the enol as the active proton donor and with the tautomerization acting as a fast equilibrium. Only in a single case addition of small amounts of base to the solution gave rise to an increase in the rate of reaction. In *Table III* are shown the values of k_{obs}(solv) calculated from the stoichiometric concentration of the acid, and in parentheses the values of k_2^{enol}(solv) calculated as $k_2^{enol}(solv) = k_{obs}(solv)^* (1 + K_9)/K_9$. From *Table III* it appears that the rate constants for the proton transfer from the enol forms of acetyl acetone and ethyl acetoacetate are almost independent of solvent, while the rate constant for the enol form of dimedone like the rate constants for phenol and benzoic acid (also shown in *Table III*) increases by almost two orders of magnitude when the solvent is changed from DMSO or DMF to MeCN [9].

TABLE II. - *Measured thermodynamic acidities in DMSO, pK, and the calculated thermodynamic acidities for the two tautomers, pK^K and pK^E.*

	pK	pK^K	pK^E
DIMH	11.2	<9.2	11.2
AAH	13.3	12.9	13.1
EAAH	14.2	14.2	12.5
PhOH	18.0		
PhCOOH	11.0		

TABLE III. - *Observed second order rate constants in $M^{-1}s^{-1}$ for protonation of anthracene anion radical at 20 °C, and in parentheses the k_2^{enol}(solv)-values in $M^{-1}s^{-1}$.*

	DMSO	DMF	MeCN
DIMH	$1.8 \cdot 10^6$	$3.6 \cdot 10^6$	$1.6 \cdot 10^8$ ($2.4 \cdot 10^8$)
AAH	$2.1 \cdot 10^4$ ($3.6 \cdot 10^4$)	$3.8 \cdot 10^4$ ($5.8 \cdot 10^4$)	$2.1 \cdot 10^4$ ($3.7 \cdot 10^4$)
EAAH	$3.8 \cdot 10^3$ ($1.9 \cdot 10^5$)	$9.8 \cdot 10^3$ ($2.5 \cdot 10^5$)	$4.0 \cdot 10^3$ ($1.0 \cdot 10^5$)
PhOH	$2.6 \cdot 10^3$	$5.4 \cdot 10^3$	$3.0 \cdot 10^5$
PhCOOH	$8.4 \cdot 10^5$	$3.0 \cdot 10^6$	$1.6 \cdot 10^8$

The effect of the hydrogen-bonding to the solvent, eqn. (10)

In order to investigate the above mentioned solvent effects in a more systematic manner, a series of phenols (phenol and mono-, di-, and trimethyl substituted phenols were applied as proton sources for protonation of anthracene anion radical in four different solvents, DMSO, DMF, PC and MeCN [10].

Values of the second order rate constants - calculated taking into account the influence of homoconjugation - are shown in *Table IV* and again demonstrate a very large change in size, when the solvent is changed from DMSO or DMF to PC or MeCN, furthermore, the kinetic range covered by the proton transfer reactions is significantly larger in PC and MeCN than in DMSO and DMF. From the Hammett plot in *Fig. 3* the striking observation is made, that the 2,6-disubstituted phenols react *faster* in DMF (and in DMSO) than predicted from the correlation of the other points, whereas this is not the case in PC (or in MeCN).

From the results found for the enol-systems above, we may conclude that the rate differences are due to differences in the hydrogen-bonding between the acid and the solvent. The question is whether the hydrogen-bond to the solvent has to be broken *before* the proton transfer takes place or breaking of the hydrogen-bond and transfer of the proton is a concerted proces. From the results discussed above obtained using the homoconjugation complex as a proton source, we find it most likely that the active proton donor is the free (non-hydrogen-bonded) phenol. This model allows a recalculation of the rate constant for the proton transfer, if the concentration of the free acid can be calculated according to eqn. (13).

$$[HB] = C^{\circ}_{HB}/(1 + K_{10}[solv])$$

TABLE IV. - *Second order rate constants, $k_2(solv)$, for the protonation of anthracene anion radical by PhOH and 13 methyl-substituted phenols calculated using theoretical data taking into account deviations from pseudo-first order conditions.*

		k_2(solv) / ($M^{-1}s^{-1}$)		
Phenol substituent	DMSO	DMF	PC	MeCN
None	3.40×10^3	6.08×10^3	1.34×10^5	2.82×10^5
2-methyl	1.54×10^3	3.30×10^3	4.64×10^4	1.32×10^5
3-methyl	2.46×10^3	3.99×10^3	7.32×10^4	2.22×10^5
4-methyl	1.45×10^3	2.25×10^3	5.50×10^4	1.28×10^5
2,3-dimethyl	9.22×10^2	1.74×10^3	2.30×10^4	7.16×10^4
2,4-dimethyl	7.89×10^2	1.25×10^3	1.62×10^4	5.73×10^4
2,5-dimethyl	1.31×10^3	1.96×10^3	3.41×10^4	9.39×10^4
2,6-dimethyl	1.38×10^3	2.36×10^3	1.89×10^4	5.72×10^4
3,4-dimethyl	1.04×10^3	1.64×10^3	2.41×10^4	9.68×10^4
3,5-dimethyl	1.66×10^3	3.31×10^3	5.34×10^4	1.45×10^5
2,3,5-trimethyl	9.47×10^2	1.21×10^3	1.48×10^4	5.34×10^4
2,3,6-trimethyl	1.13×10^3	1.75×10^3	1.19×10^4	2.70×10^4
2,4,6-trimethyl	7.30×10^2	1.45×10^3	6.12×10^3	1.49×10^4
3,4,5-trimethyl	9.91×10^2	1.24×10^3	1.43×10^4	8.46×10^4

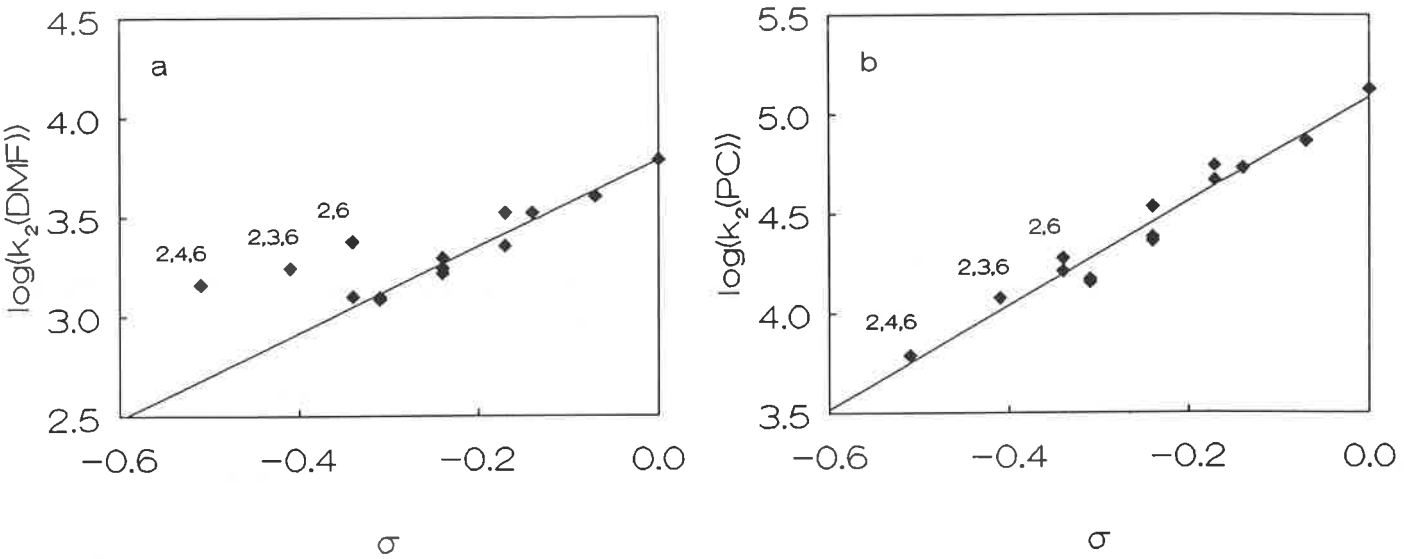

FIGURE 3. - *Hammett plots of the* $k_2(solv)$*-values in* Table IV *for (a) DMF (b) PC.*

Unfortunately, equilibrium constants for hydrogen-bonding between hydrogen-bond donors like phenols and hydrogen-bond acceptors like DMSO, DMF, PC and MeCN have not been measured with the hydrogen-bond acceptor as the solvent.

However, is has been found, [14] that the heat of hydrogen-bond formation, ΔH_f, for phenols and hydrogen-bond acceptors are practically identical, when measured in the hydrogen-bond acceptor and when measured in CCl_4 with the phenol and the hydrogen-bond acceptor as solutes, as shown in *Table V*. At the same time, the entropy of hydrogen-bond formation, ΔS_f, is practically constant for a series, when either the donor or the acceptor is kept constant [15-16]. We have therefore assumed that $K_{10}(CCl_4)$-values can be used for K_{10}.

Only 6 of the 64 K_{10}-values can be found in the literature, but from other literature values secondary values can be obtained by application of linear free energy relations of the types shown in eqns. (14) and (15), and as demonstrated in *Figs. 4 and 5*.

TABLE V. - *Data from ref. [14] for the heat of hydrogen-bond formation,* ΔH_f*, at 25 °C measured calorimetrically either by the pure base method or in dilute* CCl_4 *solution for PhOH and 4-fluoro-phenol as hydrogen-bond donors.*

H-acceptor	ΔH_f/ (kcal mol^{-1})		$K_{10}(CCl_4)$/M^{-1}		
	pure base	CCl_4	IR*	ΔH_f(pure base)**	
phenol:					
DMF	-6.86±0.08		-6.3±0.2	75.5±2.0	70.0±6.0
THF	-5.75±0.08		-5.7±0.3	13.3±0.4	13.6±0.4
Pyridine	-7.34±0.10		-7.2±0.2	49.7±1.0	48.0±2.0
4-fluoro-phenol:					
DMF	-6.97±0.11		-6.7±0.2	116.0±3.0	122±9
DMSO	-7.21±0.08		-6.6±0.1	346±8	
THF	-5.75±0.08		-6.0±0.3	17.7±0.5	19.4±1.0
Pyridine	-7.40±0.09		-7.2±0.2	75.0±1.5	74.0±5.0

* Equilibrium constant determined from IR measurements in dilute CCl_4 solution.

** Equilibrium constant calculated from calorimetrically determined ΔH_f in dilute CCl_4 at several concentrations of the hydrogen-bond donor assuming ΔH_f(pure base) equal to $\Delta H_f(CCl_4)$.

$$\log K_{10}(\text{donor}_1/\text{acceptor}_i) = c_1 \log K_{10}(\text{donor}_2/\text{acceptor}_i) + c_2 \quad (14)$$

$$\log K_{10}(\text{donor}_i/\text{acceptor}_1) = c_3 \log K_{10}(\text{donor}_i/\text{acceptor}_2) + c_4 \quad (15)$$

From applications of (14) and (15) the K_{10}-values in *Table VI* were obtained, and in the 6 cases where comparison with primary data were possible, the agreement was well.

From *Table VI* it appears that the 2,6-disubstituted phenols have relatively small K_{10}-values especially in DMSO and DMF.

Recalculation of the rate constants from *Table IV* using eqn. (13) and the K_{10}-values in *Table VI* results in the rate constants in *Table VII*, which are believed to be the best rate constants for the microscopic proton transfer step (2) ; (the rate constants in *Table VII* are also corrected for kinetic contributions from hydrogen-bonded phenol dimers which is not discussed here [10]). Three major results are apparent from *Table VII* : first, the rate constants are 2-3 orders of magnitude larger than the k_2(obs)-values in *Table IV* ; second, the effect on k_2 of changing the solvent is within approximately half an order of magnitude, and is now comparable

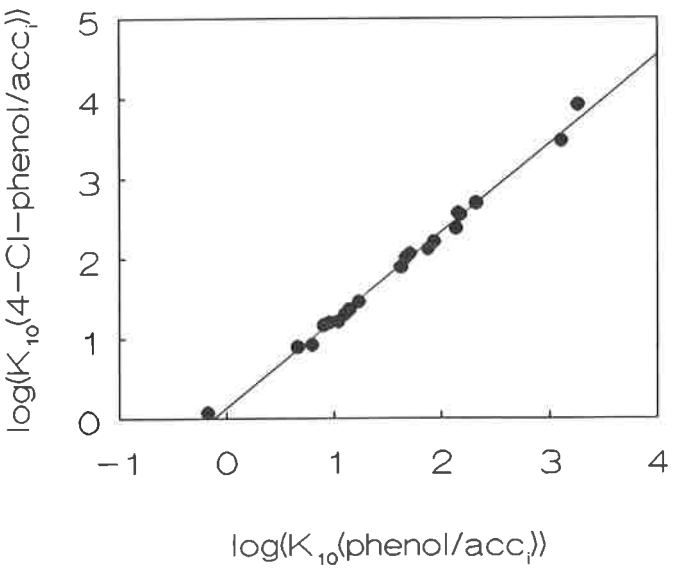

FIGURE 4. - *Plot of* K_{10}*(4-Cl-phenol/acc*$_i$*) vs.* K_{10}*(phenol/acc*$_i$*) according to eqn. (14).*

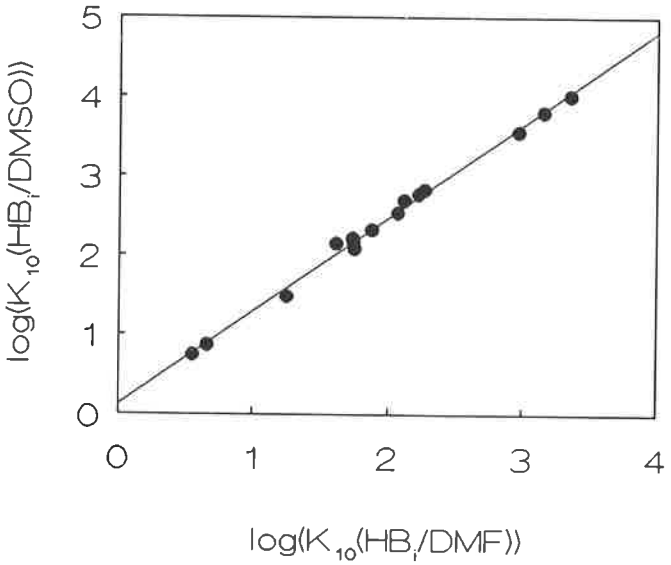

FIGURE 5. - *Plot of* $K_{10}(HB_i / DMSO)$ *vs.* $K_{10}(HB_i / DMF)$ *according to eqn. (15).*

TABLE VII. - *Second order rate constants for proton transfer to anthracene anion radical from free, monomeric phenols calculated from the data in Table IV as described in the text.*

Phenol substituent	k_2 / ($M^{-1}s^{-1}$)			
	DMSO	DMF	PC	MeCN
None	$9.9x10^6$	$5.6x10^6$	$1.5x10^7$	$2.8x10^7$
2-methyl	$2.4x10^6$	$1.9x10^6$	$3.4x10^6$	$9.3x10^6$
3-methyl	$5.5x10^6$	$2.9x10^6$	$6.7x10^6$	$1.8x10^7$
4-methyl	$3.2x10^6$	$1.6x10^6$	$5.0x10^6$	$1.0x10^7$
2,3-dimethyl	$1.1x10^6$	$7.4x10^5$	$1.4x10^6$	$4.1x10^6$
2,4-dimethyl	$9.0x10^5$	$5.3x10^5$	$9.0x10^5$	$3.3x10^6$
2,5-dimethyl	$1.6x10^6$	$8.9x10^5$	$2.1x10^6$	$5.6x10^6$
2,6-dimethyl	$4.6x10^5$	$3.5x10^5$	$5.2x10^5$	$1.8x10^6$
3,4-dimethyl	$1.6x10^6$	$8.8x10^5$	$1.5x10^6$	$6.2x10^6$
3,5-dimethyl	$2.9x10^6$	$2.0x10^6$	$4.1x10^6$	$1.0x10^7$
2,3,5-trimethyl	$9.3x10^5$	$4.4x10^5$	$7.7x10^5$	$2.8x10^6$
2,3,6-trimethyl	$3.0x10^5$	$2.2x10^5$	$2.9x10^5$	$7.3x10^5$
2,4,6-trimethyl	$1.7x10^5$	$1.6x10^5$	$1.3x10^5$	$3.8x10^5$
3,4,5-trimethyl	$1.3x10^6$	$5.2x10^5$	$5.8x10^5$	$4.7x10^6$

TABLE VI. - *Secondary values of the equilibrium constant for hydrogen-bond formation,* K_{10}*, at 25 °C between 14 phenols and the four polar aprotic solvents determined as described in the text.*

Phenol substituent	DMSO	DMF	PC	MeCN
	$K_{10}(CCl_4)/M^{-1}$			
None	210(210)	75(75)	9.2	5.1(5.1)
2-methyl	112	44	6.2	3.7
3-methyl	160(130)	60(57)	7.8	4.5
4-methyl	160(150)	60	7.7	4.5
2,3-dimethyl	84	34	5.1	3.2
2,4-dimethyl	82	34	5.0	3.2
2,5-dimethyl	89	36	5.3	3.3
2,6-dimethyl	24	12	2.3	1.6
3,4-dimethyl	110	44	6.2	3.7
3,5-dimethyl	130	50	6.8	4.0
2,3,5-trimethyl	71	30	4.6	2.9
2,3,6-trimethyl	19	9.7	2.0	1.5
2,4,6-trimethyl	17	8.8	1.8	1.4
3,4,5-trimethyl	99	40	5.7	3.5

to the solvent effects observed for e.g. S_N2-reactions ; third, the effect of methyl substitution is similar in the four solvents. Also, the Hammett plots in *Fig. 6* show that the 2,6-disubstituted phenols in DMF (and DMSO) behave "normally", when their much weaker hydrogen-bond interaction with the solvent is taken into account.

From these results we accept the model which includes dissociation of the HB/solv complex followed by proton transfer from the free HB for the protonation reaction. This model also implies that all other hydrogen-bond formations as e.g. the homoconjugation take place in competition with the hydrogen-bonding to the solvent. This allows calculation of an "intrinsic" value for the homoconjugation equilibrium constant, if the values of K_6(solv) for

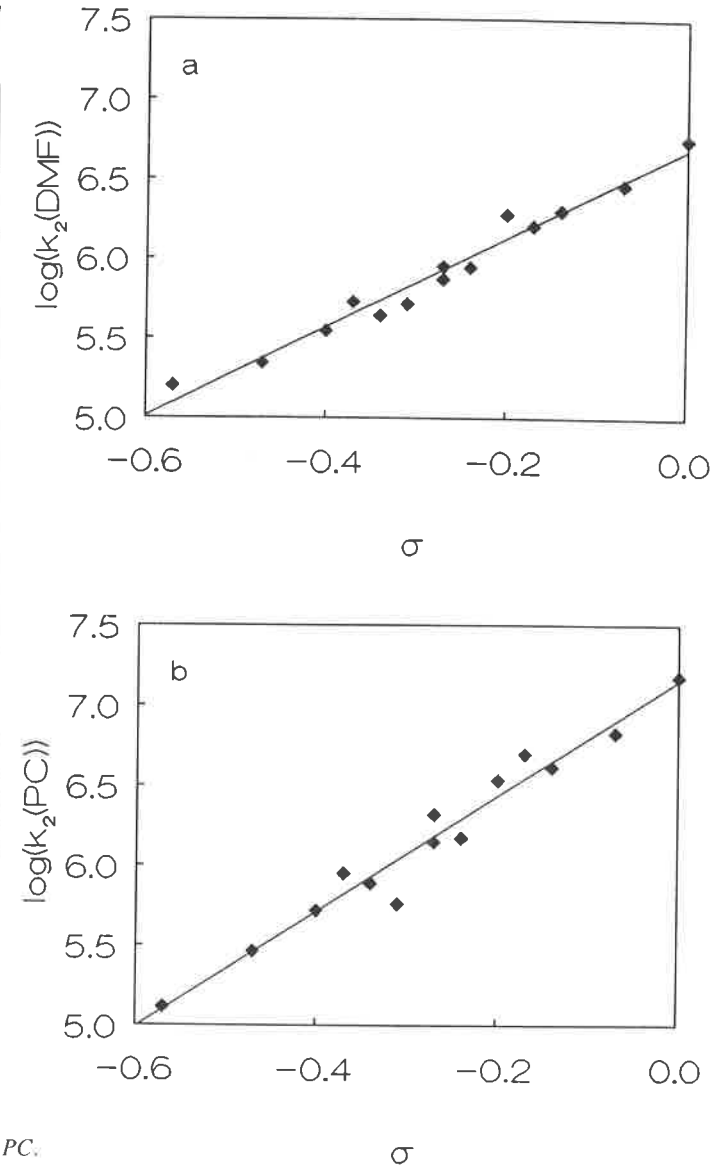

FIGURE 6. - *Hammett plots of the* k_2*-values in* Table VII *for (a) DMF (b) PC.*

the HB, B system together with $K_{10}(CCl_4)$ for the HB, solv system are known, and in fact this calculation results in constant "intrinsic" K_6-values for systems where K_6(solv) has been determined in several solvents [10].

Likewise, measured pK-values in polar aprotic solvents do not take into account that the proton donor is present in the two forms HB and HB/solv, and the pK-values must consequently be recalculated according to eqn. (16), if they are correlated with the new "intrinsic" rate constants in *Table VII*.

$$pK_{intr}(solv) = pK_{meas}(solv) - \log(1 + K_{10}[solv]) \quad (16)$$

In *Table VIII* pK-values for some of the methylsubstituted phenols measured in DMSO have been recalculated according to eqn. (16) and the appropriate K_{10}-values from *Table VI*. As a consequence, the apparent "high" acidity of 2,6-dimethyl phenol disappears, when it is taken into account, that the equilibrium constant for hydrogen-bonding between 2,6-dimethyl phenol and DMSO is much smaller than for the other phenols.

Similar corrections can be made for the other solvents, and the rate constants in *Table VII* can be correlated with the driving force for the proton transfer in a Brønsted plot. The results are summarized in *Table IX*.

TABLE VIII. - *pK_{meas} at 25 °C and pK_{intr} calculated from eqn. (16) for 5 of the phenols.*

Phenol substituent	pK_{meas}	pK_{intr}
none	18.03	14.53
2-methyl	18.10	14.89
3-methyl	18.23	14.87
4-methyl	18.86	15.51
2,6-dimethyl	18.52	15.99

TABLE IX. - *Summary of the Hammett slope, ρ, intercept (k_2 for PhOH), the regression coefficients and the Brønsted α-value for the reaction.*

	DMSO	DMF	PC	MeCN
slope, ρ	3.1	2.8	3.6	3.3
intercept	7.0	6.7	7.1	7.5
regr. coef., r	0.99	0.99	0.98	0.98
α	0.5	0.5	0.7	0.6

Conclusions

The results presented above demonstrate that high precision electrochemical methods can be used to obtain kinetic results, which together with physical chemical data from other areas, may be used to refine the mechanistic description of homogeneous chemical reactions, in this case proton transfer reactions in polar aprotic solvents.

A main conclusion derived the from results outlined above is that very great care should be taken, when reported proton transfer rate constants are used in theoretical models on a molecular level, because the reported rate constants most often include specific (microscopic) solvent effects.

Acknowledgements : We gratefully acknowledge the receipt of funds from The Carlsberg Foundation and The Danish Natural Science Research Council for purchase of the instrumentation, and from The Carlsberg Foundation for support of MFN. MFN also gratefully acknowledge Dr. Christian Amatore, Laboratoire de chimie, École Normale Supérieure, Paris, for accepting MFN as a visitor in his laboratory for a year.

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