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Kinetics of protonation of the acridine radical anion in DMF by water and alcohols

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Abstract

Rate constants k_H for the proton transfer from water, ethanol, *n*-propanol and *t*-butanol to the radical anion of acridine in DMF was measured by the voltammetric method. The Brönsted plot of log k_H against pK_a with a slope of $\alpha = -0.5$ was observed. The acidity of the conjugate acid of acridine radical anion was estimated to be in the range of $41 \gg pK_a > 24.3$. It is supported that the reaction under study is the true proton transfer contrariwise to the protonation of anthracene radical anion forming –CH acid. © 2000 Published by Elsevier Science Ltd.

Protonation of aromatic radical anions formed by electron transfer steps in a variety of organic reactions is a fundamental step in their decay. The kinetics of that reaction have been intensively investigated only for radical anions formed by aromatic hydrocarbons at electrodes in aprotic solvents with added proton donors.[1–4] In those studies it was shown that the above process occurs according to the disproportionation mechanism DISP1[5] which involves reversible electron transfer from the electrode, followed by proton transfer to a radical anion, which is the rate determining step, then a second electron transfer in solution (i.e. the disproportionation reaction) and finally a second proton transfer yielding the dihydrocompound. Homoconjugation and the formation of dimers by the proton donor should also be taken into account[6] in order to explain all of the experimental results. On the other hand, it was argued[7–9] that the proton transfer step in the deprotonation of radical cations, originally NADH analogues but also other –CH acids, should be described as concerted electron and H atom transfer and the dynamics of this process is similar to dissociative electron transfer.[10] In particular, the proposed model[7–9] explains that the intrinsic activation barrier $\Delta G_o^{\ddagger}$ (i.e. the barrier at $\Delta G^o = 0$) includes contributions from the homolytic bond dissociation enthalpy D and the solvent reorganisation energy λ_o, namely $\Delta G_o^{\ddagger} = D/4 + \lambda_o/4$. Recently, the same model has been applied[11] to the protonation of radical anions of anthracene in *N*,*N*-dimethylformamide (DMF) by a series of substituted phenols; this

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was supported by the estimation of $\Delta G_o^{\ddagger} = 59.2 \pm 0.6$ kJ mol^{-1} and $D/4 = 51$ kJ mol^{-1} (D is the enthalpy change for the homolytic dissociation of the conjugate acid to anthracene Ar and H atom: $ArH^{\cdot} \rightarrow Ar + H^{\cdot}$). On the other hand, the deprotonation of 'normal' acids, i.e. –OH and –NH acids,[12] and the reverse reaction, should be the simple proton transfer and the contribution from the bond dissociation to $\Delta G_o^{\ddagger}$ is not expected. However, the protonation of radical anions with heteroatoms in molecules is much faster and the kinetic data in aprotic solvents necessary to support the above expectation are not available. Thus, the purpose of this letter is to investigate the kinetics of protonation of the acridine radical anion in DMF using weak proton donors (DH).

Voltammetric characteristics found at 25°C for the electroreduction of 1 mM acridine at a mercury electrode in DMF containing 0.1 M tetrabutylammonium perchlorate (TBAP) in the presence of DH indicate the DISP1 mechanism: shifts of the peak potential E_p with the scan rate ν and with the donor concentration are close to theoretical values.[5] The bimolecular rate constant k_H for protonation was obtained from the pseudo-first order rate constant determined under the excess of DH (cf. Table 1) by fitting to the theoretical curve the experimental shift of E_p values with ν, as previously described.[11]

Table 1
The concentration range and the acidity of proton donors used and rate constants for the protonation of acridine radical anion in DMF at 25°C

Proton donor	C_{DH} /mmol dm^{-3}	pK_a^{DMF}	M[a]	Log (k_H /mol^{-1} dm^3 s^{-1})
t-BuOH	76 – 152	32.5	42	1.78±.03
H_2O	55 – 166	31.5	76	2.35±.02
n-PrOH	53 – 160	≅31	86	2.55±.02
EtOH	119 - 187	30.2	22	2.8±.1

[a]Number of measurements.

The k_H values obtained and their errors estimated from Student's distribution with a confidence level of 0.95 are collected in Table 1. The number of measurements M indicates the total number of voltammograms at different scan rates and DH concentrations. Equilibrium acidities in DMF of DH used, pK_a^{DMF} are also given in Table 1. For *t*-BuOH, water and EtOH they were obtained from pK_a values determined in dimethyl sulfoxide (DMSO) by Bordwell,[13,14] using an equation proposed by Maran et al.[15] The value of pK_a^{DMF} for *n*-PrOH was estimated from a comparison of the pK_a of water and a few alcohols (including 2-propanol and methanol) with the corresponding enthalpies of deprotonation obtained in DMSO by Arnett.[16]

It is evident from Table 1 that the rate constants measured depend on the acidity of DH used. The linear Brönsted plot holds with the correlation coefficient of $r = 0.9879$ and the slope of $\alpha = -0.5 \pm .2$, as is shown in Fig. 1. The obtained slope indicates that the process of interest is under activation control and that a region of 'counter diffusion' control, where the backward reaction to the protonation step reaches the diffusion limit and $\alpha = -1.0$, can be expected at much higher pK_a^{DMF} values.[12,17] Thus, assuming the protonation rate constant for the bimolecular diffusion control $\log k_D = 10$ (estimated on the basis of the Smoluchowski–Debye equation[17]), it is possible to evaluate the lower limit of acidity of the conjugate acid of the acridine radical anion $AH^{\cdot}$ in

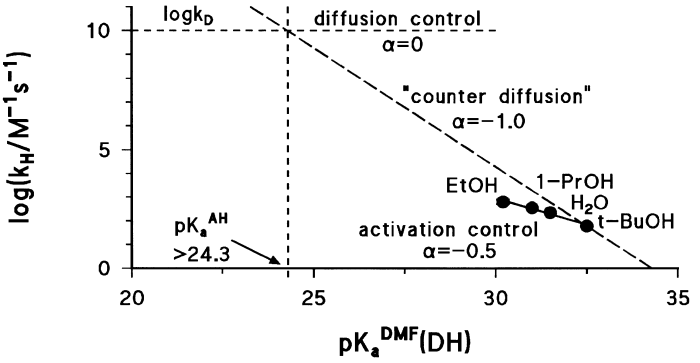

Figure 1. Brönsted plot for the protonation of acridine radical anion in DMF and the procedure for determining the lower limit of acidity of its conjugate acid

DMF, as shown in Fig. 1. The resulting limit of $pK_a^{AH} > 24.3$ looks reasonable, taking into account the fact that the acridine radical anion should be more basic than the radical anion of anthracene, the conjugate acid of which has $pK_a^{DMF} = 21$.[11] It is more difficult to estimate the upper limit of pK_a^{AH} but one can safely expect that the NH_2^- anion is much more basic in aprotic solvents than acridine radical anion because of a greater localisation of a negative charge at the nitrogen atom (due to two lone electron pairs and smaller size). The last conclusion is fully supported by the electrochemical behaviour of acridine radical anions in ammonia at room temperature and a higher pressure.[18] Thus, pK_a^{AH} should be much smaller than pK_a of NH_3, the conjugate acid of the NH_2^- anion; for NH_3 in DMF $pK_a \cong 41$ was calculated from data in DMSO.[13] Finally, for the conjugate acid of acridine radical anion $AH^{\cdot}$ the obtained acidity range is: $41 > > pK_a^{AH} > 24.3$.

For the reaction considered, the Gibbs' free energy of activation $\Delta G^{\ddagger}$ can be obtained from the rate constants (Table 1) assuming[7–9,11] the collision frequency $Z = 3 \times 10^{11}$ mol^{-1} dm^3 s^{-1}, neglecting the work terms[7–9,11] and taking into account the usual equations: $\Delta G^{\ddagger} = \Delta G_o^{\ddagger} + 0.5\Delta G^o + (\Delta G^o)^2/16\Delta G_o^{\ddagger}$ and $\Delta G^o = 2.3$ RT $(pK_a^{DH} - pK_a^{AH})$. The enthalpy of bond breaking D can be calculated[7,11] from the thermodynamic cycle proper for the reaction $AH^{\cdot}_{DMF} \rightarrow A_{DMF} + H^{\cdot}_{gas}$ as $D = 2.892 + 0.059pK_a^{AH} + E^o(A/A^{\cdot-})$, where $E^o(A/A^{\cdot-}) = -1.56$ V versus SCE is the formal potential for the couple: acridine/its radical anion. For the proposed range of pK_a^{AH} from 24.3 to 41 the intrinsic activation barrier $\Delta G_o^{\ddagger}$ increases from 28 to 77 kJ mol^{-1} but the contribution from bond breaking D/4 increases from 65 to 89 kJ mol^{-1}, respectively. Then it is evident that D/4 is higher than $\Delta G_o^{\ddagger}$ and the bond cleavage energy does not contribute to the activation barrier but the protonation of acridine radical anion in DMF is the true proton transfer.

Experimental: Acridine from Schuchardt (Germany) was purified by vacuum sublimation. Triple-distilled water was used. Ethanol 99.8% from POCh (Poland) was dried by treatment with magnesium; *t*-butanol A.R. from Fluka, *n*-propanol A.R. from Ubichem and DMF from Merck (Uvasol grade, containing 0.028% of water) were used as received. Voltammetric curves at 25±1°C were recorded with a PAR 273A potentiostat controlled by an IBM PC AT computer by means of the software M270 from PAR. A three-electrode cell was used consisting of a static mercury drop electrode (SMDE, Laboratorni Pristroje, Prague), a Pt counter electrode and Ag/Ag^+ couple in acetonitrile as the reference electrode.

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