Thermochimica Acta, 66 (1983) 377–382
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

ACID DISSOCIATION CONSTANTS OF MONOBROMOANILINIUM IONS IN FORMAMIDE

KANCHAN ACHARYA and BIMBADHAR NAYAK

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302 (India)

(Received 4 February 1983)

In a recent communication [1], we reported the acid dissociation constants of anilinium ions as well as the three mononitroanilinium ions in formamide over the temperature range 10–50°C (283.15–323.15 K) as determined from e.m.f. measurements using cells of the type

$$\mathrm{Pt, H_2/B}(m_1)\mathrm{, BHCl}(m_2)\mathrm{/AgCl{-}Ag} \qquad \text{(A)}$$

where B represents the base. It was also reported that the values of dissociation constants at 25°C (298.15 K) as determined from the cells of the type (A) also agreed well with those obtained from e.m.f. measurements of cells of the type

$$\mathrm{Pt, Q{-}QH_2/B}(m_1)\mathrm{, BHCl}(m_2)\mathrm{/AgCl{-}Ag} \qquad \text{(B)}$$

The acid dissociation constants of monobromoanilinium ions in formamide at several temperatures following the same procedure and using cells of the same types are reported in this paper. This is in accordance with the general programme in this laboratory to study different types of ionic equilibria in formamide, a solvent having a dielectric constant higher than that of water.

EXPERIMENTAL

The bromoaniline samples studied were all obtained commercially. *Ortho* and *m*-bromoanilines were purified by vacuum distillation and *p*-bromoaniline was recrystallized from dilute ethanol to constant melting point. The procedure for the preparation of the hydrochlorides of the bases and their purification were described earlier [1]. The purity of the bases and their hydrochlorides was checked by boiling point and melting point measurements as appropriate. All the chemicals were stored in desiccators over Drierite until required. Formamide (S.D.'S, LR) was purified as described earlier by Dash and Nayak [2].

The preparation of the solutions for e.m.f. measurements, filling and

0040-6031/83/$03.00

setting up of cells (A) and (B), thermostatting of the solutions and measurements of e.m.f. were all similar to those described earlier [1,3].

All measurements were reduced to 760 mm pressure. The vapour pressure of formamide was estimated to be less than 10 mm at temperatures below 60°C (333.15 K) from data available in the literature. In most cases the correction for barometric pressure was found to be negligible.

RESULTS AND DISCUSSION

The dissociation constants were obtained by the method based on the evaluation of apparent hydrogen ion molality, $m'(\mathrm{H}^+)$, as described in an earlier communication [1]. The acid dissociation constant, K_a, of the conjugate acid is related to the e.m.f., E, of cells (A) and (B) through the equation

$$\frac{F(E-E^0)}{2.303RT}+\log\frac{m(\mathrm{BH}^+)\,m(\mathrm{Cl}^-)}{m(\mathrm{B})}=-\log K_a-\log\frac{\gamma(\mathrm{BH}^+)\,\gamma(\mathrm{Cl}^-)}{\gamma(\mathrm{B})} \tag{1}$$

where m and γ are, respectively, the molalities and the activity coefficients of the species shown in parentheses.

The left-hand side of eqn. (1), which may be represented by $-\log K_a'$, is evaluated using the equation

$$-\log K_a'=-\log\frac{m'(\mathrm{H}^+)[m_1+m'(\mathrm{H}^+)]}{m_2-m'(\mathrm{H}^+)} \tag{2}$$

where $m'(\mathrm{H}^+)$ is approximately given by the relation

$$-\log m'(\mathrm{H}^+)=\frac{F(E-E^0)}{2.303RT}+\log m_2-2A\sqrt{\mu d_0} \tag{3}$$

Extrapolation of $-\log K_a'$ to $\mu=0$ yields $-\log K_a$, since under this condition, the difference between K_a and K_a', if any, vanishes. The pK_a values obtained by this procedure over the temperature range 10–50°C (283.15–323.15 K) are shown in Table 4 along with the standard deviations calculated by the method of least squares.

Typical e.m.f. readings of cell (A) and (B) and other data needed for the computation of $-\log K_a$ at 25°C (298.15 K) are shown in Tables 1–3.

A comparison of the present pK_a data with the corresponding values in water [5–7] shows that the pK_a values are higher in formamide than in water, which is in complete agreement with our previous observation [1] and with the general behaviour of the conjugate acids of bases and of weak acids in solvents of this class [3,4,10–12]. The pK_a values obtained for these conjugate acids at 25°C (298.15 K) with cell (B) are slightly higher than those obtained with cell (A) (Table 5). Considering the supposed limitations of the quinhydrone electrode in media containing amines, this agreement is quite

TABLE 1

Determination of $-\log K_a$ of the *o*-bromoanilinium ion (*o*-BrAnH$^+$) in formamide at 25°C (298.15 K)

10^2m_1 (mole kg^{-1})	$10^2m_2 = 10^2\mu$[a] (mole kg^{-1})	E (V)	$\frac{F(E-E^0)}{2.303RT}$	$2A\sqrt{\mu d_0}$	$10^4m'(\mathrm{H}^+)$ (mole kg^{-1})	$-\log K_a'$	$-\log K_a$
From the study of cell (A)							
1.088	0.526	0.5220	5.4703	0.0473	7.170	2.7375	3.00 ± 0.08
0.992	0.604	0.5195	5.4280	0.0507	6.936	2.8611	
1.446	0.853	0.5015	5.1238	0.0603	10.117	2.6815	
1.605	0.912	0.5054	5.1897	0.0623	8.168	2.7801	
1.668	1.045	0.4885	4.9040	0.0667	13.902	2.5571	
1.958	1.218	0.4850	4.8449	0.0720	13.837	2.5708	
From the study of cell (B)							
0.975	0.566	−0.1898	5.5044	0.0491	6.194	2.8947	3.15 ± 0.12
1.416	0.732	−0.1876	5.5416	0.0558	4.464	3.0229	
1.392	0.869	−0.1980	5.3658	0.0608	5.702	2.9925	
1.614	1.022	−0.2125	5.1207	0.0660	8.612	2.8056	
1.819	1.150	−0.2210	4.9770	0.0700	10.770	2.7010	
1.896	1.225	−0.2148	5.0818	0.0722	8.013	2.8591	

[a] μ = Ionic strength of the medium.

TABLE 2

Determination of $-\log K_a$ of the *m*-bromoanilinium ion (*m*-BrAnH$^+$) in formamide at 25°C (298.15 K)

10^2m_1 (mole kg^{-1})	$10^2m_2 = 10^2\mu$ (mole kg^{-1})	E (V)	$\frac{F(E-E^0)}{2.303RT}$	$2A\sqrt{\mu d_0}$	$10^5m'(\mathrm{H}^+)$ (mole kg^{-1})	$-\log K_a'$	$-\log K_a$
From the study of cell (A)							
0.980	0.514	0.5840	6.5183	0.0468	6.558	3.8945	3.96 ± 0.08
1.086	0.645	0.5648	6.1938	0.0524	11.178	3.7133	
1.554	0.858	0.5635	6.1718	0.0605	9.004	3.7805	
1.705	0.952	0.5585	6.0873	0.0637	9.932	3.7428	
1.686	1.074	0.5440	5.8422	0.0677	15.623	3.6000	
1.945	1.216	0.5478	5.9064	0.0720	12.021	3.7091	
From the study of cell (B)							
1.069	0.582	−0.1295	6.5238	0.0498	5.769	3.9682	4.05 ± 0.11
1.339	0.736	−0.1448	6.2651	0.0560	8.395	3.8084	
1.546	0.872	−0.1350	6.4308	0.0609	4.894	4.0584	
1.668	0.908	−0.1438	6.2820	0.0622	6.640	3.9088	
1.890	1.133	−0.1580	6.0420	0.0695	9.426	3.7975	
2.016	1.305	−0.1605	5.9997	0.0746	9.122	3.8414	

TABLE 3

Determination of $-\log K_a$ of the *p*-bromoanilinium ion (*p*-BrAnH$^+$) in formamide at 25°C (298.15 K)

$10^2 m_1$ (mole kg^{-1})	$10^2 m_2 = 10^2 \mu$ (mole kg^{-1})	E (V)	$\frac{F(E-E^0)}{2.303RT}$	$2A\sqrt{\mu d_0}$	$10^5 m'(\mathrm{H}^+)$ (mole kg^{-1})	$-\log K'_a$	$-\log K_a$
From the study of cell (A)							
0.986	0.492	0.6066	6.9004	0.0458	2.841	4.2407	4.29 ± 0.06
1.166	0.625	0.5928	6.6671	0.0516	3.878	4.1361	
1.365	0.782	0.5826	6.4947	0.0577	4.667	4.0849	
1.748	0.936	0.5875	6.5775	0.0632	3.263	4.2128	
1.926	1.048	0.5784	6.4237	0.0668	4.188	4.1110	
2.056	1.225	0.5690	6.2648	0.0723	5.231	4.0536	
From the study of cell (B)							
1.038	0.516	−0.1085	6.8787	0.0469	2.855	4.2360	4.42 ± 0.06
1.288	0.725	−0.1190	6.7013	0.0556	3.119	4.2532	
1.556	0.844	−0.1266	6.5728	0.0599	3.638	4.1701	
1.668	0.952	−0.1385	6.3716	0.0637	5.170	4.0393	
1.850	1.022	−0.1330	6.4646	0.0660	3.907	4.1397	
1.968	1.218	−0.1456	6.2516	0.0720	5.462	4.0511	

satisfactory and confirms our earlier suggestion [1] that the quinhydrone electrode behaves more satisfactorily in formamide than in water, even in the presence of amines.

A comparison of the pK_a values of monobromoanilinium ions at 25°C (298.15 K) in different solvents (Table 5) shows that in general, the pK_a values are not linearly related to $1/D$ (where D is the dielectric constant of

TABLE 4

Effect of temperature on $-\log K_a$ from the study of cell (A) in formamide

Temperature (°C)	$-\log K_a$		
	o-BrAnH$^+$	*m*-BrAnH$^+$	*p*-BrAnH$^+$
10	3.15 ± 0.11	4.09 ± 0.13	4.28 ± 0.07
15	3.05 ± 0.08	4.02 ± 0.05	4.38 ± 0.06
20	3.01 ± 0.12	4.06 ± 0.12	4.33 ± 0.05
25	3.00 ± 0.08 (3.15 ± 0.12) [a]	3.96 ± 0.08 (4.05 ± 0.11) [a]	4.29 ± 0.06 (4.42 ± 0.06) [a]
30	2.79 ± 0.11	3.90 ± 0.09	4.20 ± 0.05
35	2.94 ± 0.09	3.78 ± 0.10	4.10 ± 0.06
40	2.92 ± 0.08	3.84 ± 0.11	3.90 ± 0.15
45	2.80 ± 0.03	3.68 ± 0.06	4.00 ± 0.04
50	2.80 ± 0.02	3.69 ± 0.04	3.98 ± 0.06

[a] Values in parentheses are from the study of cell (B).

TABLE 5

pK_a values of monobromoanilinium ions in different solvents at 25°C (298.15 K)

Ion	Water, $D = 78.54$ (refs. 5–7)	Formamide, $D = 109.5$ (present work)	Acetic acid, $D = 6.2$ (ref. 8)
o-BrAnH$^+$	2.53	3.00 (3.15) [a]	0.90
m-BrAnH$^+$	3.53	3.96 (4.05) [a]	1.93
p-BrAnH$^+$	3.89	4.29 (4.42) [a]	2.20

[a] Values in parentheses are from the study of cell (B).

the medium) as suggested by the Born equation, although they seem to depend to a large extent on the dielectric constant of the medium. The fact that the pK_a values of these conjugate acids are higher in formamide than in water even though the latter has a lower dielectric constant may be due to the lower basicity of formamide compared to that of water as already pointed out by Dash and Nayak [13].

The pK_a values of these conjugate acids decrease with increase of temperature (Table 4) although there are some irregularities; this is in agreement with earlier observations [1,3,4]. These could be, as suggested earlier, due to minute structural changes in the solvent with change of temperature.

The thermodynamic properties, ΔG^0, ΔH^0 and ΔS^0 have been evaluated as described earlier [1] on the assumption that ΔH^0 does not change appreciably over the temperature range used. The plots of log K_a vs. $1/T$ are linear thereby implying that the assumption is reasonable. The results are shown in Table 6 with similar data for aqueous medium available in

TABLE 6

Standard thermodynamic values for the dissociation process $BH^+ \rightleftharpoons B + H^+$ in formamide and water at 25°C (298.15 K)

Base (B)	ΔG^0 (kJ mole^{-1})		ΔH^0 (kJ mole^{-1})		ΔS^0 (J K^{-1} mole^{-1})	
	Water	Formamide [a]	Water	Formamide [a]	Water	Formamide [a]
o-Bromoaniline	14.40 [b]	17.13	24.27 [b]	13.97	33.06 [b]	−10.60
m-Bromoaniline	20.10 [c]	22.61	26.12 [c]	18.76	20.15 [c]	−12.91
p-Bromoaniline	22.17 [d]	24.49	28.02 [d]	19.61	19.60 [d]	−16.37
Aniline	26.20 [e]	29.11 [f]	30.84 [e]	27.28 [f]	15.57 [e]	−6.14 [f]

[a] Present work. [b] Ref 5. [c] Ref. 6. [d] Ref. 7. [e] Ref. 9. [f] Ref. 1.

literature. The values for the anilinium ion are also shown in the same table for the sake of comparison. It is seen that the order remains the same in both solvents in going from *o*-bromoaniline to *p*-bromoaniline. Also, it is found that the heat of dissociation decreases in formamide even though the free energy of dissociation increases. This is due to the lower entropy of dissociation in formamide than in water. In fact, the entropies of dissociation for these bases assume significantly negative values in formamide while they have positive values in water. These results are similar to those observed in the cases of *p*-toluidine and *p*-hydroxyaniline [3] as well as in the cases of *m*-toluidine and *p*-anisidine [4], but are in disagreement with those of nitroanilines [1] where the ΔS^0 values were found to be positive in formamide medium. The entropy change for dissociation, therefore, as has been commented upon earlier, is both solvent and substrate dependent and consequently unpredictable. However, in the cases of the bromoanilines studied, the dissociation process has a net structure-making effect in formamide while it has a structure-breaking effect in water.

REFERENCES

1 K. Acharya and B. Nayak, Electrochim. Acta, in press.
2 U.N. Dash and B. Nayak, Indian J. Chem., 8 (1970) 659.
3 S. Mukhopadhyay and B. Nayak, Electrochim. Acta 25 (1980) 807.
4 S. Mukhopadhyay and B. Nayak, Thermochim. Acta, 40 (1980) 433.
5 P.D. Bolton and F.M. Hall, J. Chem. Soc. B, 6 (1969) 1047.
6 P.D. Bolton and F.M. Hall, Aust. J. Chem., 21 (1968) 939.
7 P.D. Bolton and F.M. Hall, J. Chem. Soc. B, (1969) 259.
8 N.F. Hall, J. Am. Chem. Soc., 52 (1930) 5115.
9 P.D. Bolton and F.M. Hall, Aust. J. Chem., 20 (1967) 1797.
10 U.N. Dash and B. Nayak, Aust. J. Chem., 28 (1975) 793.
11 U.N. Dash and B. Nayak, Aust. J. Chem., 25 (1972) 941.
12 U.N. Dash and B. Nayak, Aust. J. Chem., 26 (1973) 111.
13 U.N. Dash and B. Nayak, Aust. J. Chem., 28 (1975) 1377.