

## Enthalpies of Ionization deduced from the Temperature Dependence of Indicator Measurements for Amides in Concentrated Aqueous Solutions of Perchloric Acid

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The acidity function  $H_A$  has been deduced as a function of temperature from measurements of the extent of protonation of three amides in concentrated aqueous solutions of perchloric acid. Enthalpies of dissociation of the conjugate acids of the amides have been evaluated as a function of perchloric acid concentration. The enthalpy data are in accord with theories in which acidity function behaviour is largely attributed to the release of water of hydration which occurs when a weak base combines with a proton to give its conjugate acid. The relationship between the present results and previous enthalpy data for primary amine bases is qualitatively consistent with the differences which exist between the variations with acid concentration of the  $H_A$  and  $H_0$  acidity function scales.

ENTHALPIES of dissociation of the anilinium ions conjugate to six Hammett primary amine bases in aqueous perchloric acid solutions have recently been shown to be in accord with theories in which the  $H_0$  acidity function is correlated with the activity or concentration of water in concentrated acid solutions.<sup>1</sup> Thus correlations between the enthalpy data and relative partial molar

enthalpies of water in the acid solutions are consistent with the hypothesis that the high acidity of concentrated aqueous solutions of strong acids may be largely explained by the release of water molecules of hydration which occurs when a weakly basic solute species B is

<sup>1</sup> S. A. Attiga and C. H. Rochester, *J.C.S. Perkin II*, 1974, 1624.

protonated to give  $\text{BH}^+$ . Studies of the protonation of amide bases in aqueous perchloric acid have established an  $H_A$  acidity function which differs significantly from the corresponding  $H_0$  function defined by using primary amine indicators.<sup>2,3</sup> The difference is in the sense that would require that the number of water molecules of hydration released when an amide is protonated in a particular acid solution is smaller than the number released when a primary amine is protonated in the same solution.<sup>4</sup> The present work is concerned with testing whether this requirement is substantiated by a comparison of the enthalpies of dissociation of the conjugate acids of amides and primary amines in concentrated aqueous acid solutions. Enthalpies of dissociation of the conjugate acids of 4-methoxybenzamide, 3,4,5-trimethoxybenzamide, and 3-nitrobenzamide have been deduced from measurements of the extent of protonation of the three amides in aqueous perchloric acid solutions at four temperatures.

#### EXPERIMENTAL

4-Methoxy-, 3,4,5-trimethoxy-, and 3-nitrobenzamide were recrystallized to constant m.p. from water. Stock solutions of the amides in water were prepared by weight. AnalaR aqueous 71–73 w/w % perchloric acid was diluted with water as required and was estimated volumetrically.

Spectral measurements involving solutions of the amides in aqueous perchloric acid were made using a Unicam SP 8000 spectrophotometer with 1 cm silica cells contained in a cell block which was thermostatically controlled by water circulation. Temperatures ( $\pm 0.13$  K) were monitored with a chromel–alumel thermocouple inserted into the sample cell. Spectra were recorded against blank solutions containing aqueous perchloric acid in the reference cell. The temperature cycle procedure employed previously<sup>1</sup> was not adopted because of the possibility that irreversible hydrolytic reactions would occur during the time when measurements on a particular solution were being made.<sup>3</sup> Instead a fresh solution at a particular molality of perchloric acid was prepared for each spectrophotometric determination at a series of arbitrary temperatures in the range 285–320 K. Optical density values corresponding to the temperatures 288, 298, 308, and 318 K were read off from the observed linear plots of absorbance at a particular wavelength against temperature. Wavelengths chosen for study corresponded to the absorption maxima of the conjugate acids of the amides and were 283 nm for 4-methoxy- and for 3,4,5-trimethoxybenzamide and 230 nm for 3-nitrobenzamide. Ionization ratios  $I = (C_{\text{BH}^+}/C_{\text{B}})$  where  $C_{\text{BH}^+}$  and  $C_{\text{B}}$  are the equilibrium concentrations of protonated amide and neutral amide, respectively, were deduced by the standard method.<sup>3</sup>

#### RESULTS

Ionization ratios for three amides as a function of perchloric acid concentration and at four temperatures are given in Table 1. Values of  $\text{p}K_{\text{BH}^+}$  (Table 2), where  $K_{\text{BH}^+}$  is the acid dissociation constant of a protonated amide, were deduced by the standard procedure<sup>3</sup> involving comparison of the ionization ratios of suc-

cessively weaker bases in overlapping ranges of perchloric acid concentration. The results were referred to pure water standard state *via* the corresponding protonation data<sup>1</sup> for the primary amine indicator

TABLE 1

Values of  $\log_{10}(C_{\text{BH}^+}/C_{\text{B}})$  as a function of perchloric acid concentration for three amides at four temperatures

$m/\text{mol kg}^{-1}$	288 K	298 K	308 K	318 K
(a) 4-Methoxybenzamide				
1.70	-0.94	-0.94	-0.94	-0.93
2.00	-0.82	-0.82	-0.82	-0.81
2.75	-0.51	-0.50	-0.50	-0.50
3.71	-0.22	-0.22	-0.21	-0.21
4.75	0.03	0.03	0.03	0.03
5.69	0.27	0.27	0.27	0.27
6.80	0.50	0.50	0.50	0.49
8.00	0.71	0.70	0.70	0.69
8.91	0.92	0.90	0.89	0.87
(b) 3,4,5-Trimethoxybenzamide				
5.69	-0.07	-0.06	-0.06	-0.05
6.32	0.07	0.07	0.07	0.07
6.80	0.20	0.20	0.20	0.21
7.30	0.33	0.33	0.32	0.32
8.00	0.46	0.45	0.45	0.45
8.35	0.57	0.57	0.56	0.56
8.91	0.69	0.69	0.68	0.68
9.30	0.80	0.79	0.78	0.76
9.75	0.93	0.91	0.89	0.87
(c) 3-Nitrobenzamide				
8.00	-0.20	-0.20	-0.20	-0.20
8.35	-0.08	-0.08	-0.08	-0.08
8.91	0.03	0.03	0.03	0.03
9.30	0.14	0.14	0.13	0.13
9.75	0.26	0.27	0.25	0.25
10.35	0.39	0.39	0.36	0.35
10.90	0.51	0.51	0.49	0.47
11.50	0.63	0.62	0.58	0.55
12.00	0.73	0.72	0.67	0.61
12.61	0.82	0.80	0.76	0.73
13.02	0.93	0.89	0.84	0.80
13.60	1.00	0.96	0.91	0.86
14.20	1.08	1.01	0.96	0.90

TABLE 2

Values of  $\text{p}K_{\text{BH}^+}$  for the conjugate acids of three amides in water at four temperatures

Amide	288 K	298 K	308 K	318 K
4-Methoxybenzamide	-1.56	-1.54	-1.53	-1.54
3,4,5-Trimethoxybenzamide	-1.84	-1.82	-1.80	-1.80
3-Nitrobenzamide	-2.48	-2.49	-2.44	-2.42

2-nitroaniline in aqueous perchloric acid solutions. The use of 2-nitroaniline as the reference indicator for the calculation of  $\text{p}K_{\text{BH}^+}$  values from protonation data for amides in aqueous solutions of strong acids is in accord with the procedure previously adopted by Yates *et al.*<sup>2</sup>

The amide acidity functions  $H_A$  were calculated from the  $\text{p}K_{\text{BH}^+}$  values for the amides and the corresponding ionization ratios *via* equation (i). The results for all

$$H_A = \text{p}K_{\text{BH}^+} - \log_{10}(C_{\text{BH}^+}/C_{\text{B}}) \quad (\text{i})$$

three amides at a particular temperature were plotted on a single graph and  $H_A$  values at 0.5 mol  $\text{kg}^{-1}$  intervals of perchloric acid concentration were taken from a smooth

<sup>2</sup> C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

<sup>4</sup> K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42**, 1957.

<sup>2</sup> K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418.

curve through the experimental points. The  $H_A$  scales at four temperatures are given in Table 3. Corresponding values of  $H_A$  deduced from the results of Yates

$\text{mol}^{-1}$ , and  $\pm 2.5 \text{ J K}^{-1} \text{ mol}^{-1}$  for the free energies, enthalpies, and entropies, respectively.

TABLE 3

$H_A$  Acidity function scales for aqueous perchloric acid at four temperatures (figures are for  $-H_A$ )

$m/\text{mol kg}^{-1}$	288 K	298 K	298 K <sup>a</sup>	308 K	318 K
2.0	0.78	0.78	0.78	0.78	0.78
2.5	0.98	0.98	0.97	0.98	0.98
3.0	1.15	1.15	1.15	1.14	1.14
3.5	1.30	1.29	1.30	1.29	1.29
4.0	1.42	1.42	1.42	1.41	1.41
4.5	1.53	1.52	1.54	1.51	1.52
5.0	1.63	1.62	1.67	1.62	1.61
5.5	1.74	1.73	1.78	1.72	1.72
6.0	1.85	1.84	1.89	1.83	1.82
6.5	1.97	1.95	2.00	1.94	1.93
7.0	2.08	2.07	2.10	2.06	2.05
7.5	2.20	2.18	2.22	2.17	2.15
8.0	2.32	2.31	2.33	2.29	2.27
8.5	2.45	2.43	2.59	2.41	2.38
9.0	2.57	2.55	2.71	2.53	2.50
9.5	2.69	2.67	2.73	2.64	2.60
10.0	2.80	2.77	2.83	2.74	2.71
10.5	2.92	2.90	2.94	2.86	2.82
11.0	3.03	3.01	3.04	2.96	2.91
11.5	3.13	3.11	3.14	3.05	2.99
12.0	3.21	3.20	3.22	3.13	3.07
12.5	3.31	3.28	3.28	3.21	3.15
13.0	3.40	3.37	3.34	3.28	3.22
13.5	3.48	3.43	3.39	3.36	3.28
14.0	3.54	3.50	3.46	3.42	3.33

<sup>a</sup>  $H_A$  Scale of Yates *et al.*<sup>2</sup> for aqueous  $\text{HClO}_4$  at 298 K.

*et al.*<sup>2</sup> who studied the protonation of eight amide bases in aqueous perchloric acid at 298 K are included in Table 3 for comparison with the present scale at that temperature.

Standard free energies, enthalpies, and entropies of dissociation of the conjugate acids of 4-methoxy-, 3,4,5-trimethoxy-, and 3-nitro-benzamide in water were deduced from the  $pK_{\text{BH}^+}$  data (Table 2) as before.<sup>1</sup> The results are given in Table 4. Enthalpies of dissociation of the conjugate acids in solutions containing a finite concentration of perchloric acid were calculated from equation (ii), in which values of  $C_{\text{BH}^+}/C_{\text{B}}$  were taken at

$$\Delta H = -2.303R d \log_{10}(C_{\text{BH}^+}/C_{\text{B}})/d(1/T) \quad (\text{ii})$$

constant molality of perchloric acid. The values of  $\Delta H$  as a function of perchloric acid concentration are given in

TABLE 4

Values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  for the dissociation of the conjugate acids of three amides in water at 298 K

Amide	$\frac{\Delta G^0}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^0}{\text{kJ mol}^{-1}}$	$\frac{\Delta S^0}{\text{J K}^{-1} \text{ mol}^{-1}}$
4-Methoxybenzamide	-8.80	-1.11	25.8
3,4,5-Trimethoxybenzamide	-10.36	-2.22	27.3
3-Nitrobenzamide	-14.18	-3.39	36.2

Table 5. The limits of error of the thermodynamic data in Tables 4 and 5 are within  $\pm 0.06 \text{ kJ mol}^{-1}$ ,  $\pm 0.8 \text{ kJ}$

<sup>5</sup> K. Yates and J. C. Riordan, *Canad. J. Chem.*, 1965, **43**, 2329.

<sup>6</sup> C. R. Smith and K. Yates, *J. Amer. Chem. Soc.*, 1971, **93**, 6578.

TABLE 5

Enthalpies of dissociation at 298 K of the conjugate acids of three substituted benzamides as a function of the concentration of perchloric acid in the aqueous solutions in which the dissociation occurs

$\frac{m_{\text{HClO}_4}}{\text{mol kg}^{-1}}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{m_{\text{HClO}_4}}{\text{mol kg}^{-1}}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\frac{m_{\text{HClO}_4}}{\text{mol kg}^{-1}}$	$\frac{\Delta H}{\text{kJ mol}^{-1}}$
(a) 4-Methoxybenzamide					
1.70	-0.50	3.71	-0.29	6.80	0.58
2.00	-0.50	4.75	0.00	8.00	1.13
2.75	-0.29	5.69	0.00	8.91	2.61
(b) 3,4,5-Trimethoxybenzamide					
5.69	-0.87	7.30	0.09	8.91	0.99
6.32	-0.41	8.00	0.58	9.30	2.32
6.81	-0.46	8.35	0.87	9.75	3.48
(c) 3-Nitrobenzamide					
8.35	0.00	10.35	2.18	12.61	5.39
8.91	-0.29	10.90	2.32	13.02	7.40
9.30	0.44	11.50	4.35	13.60	8.41
9.75	0.87	12.00	5.22	14.20	10.12

## DISCUSSION

The values of  $pK_{\text{BH}^+}$  at 298 K in Table 2 are in good agreement with previous values of  $-1.54$ ,<sup>2</sup>  $-1.46$ ,<sup>5</sup> and  $-1.44$ ,<sup>4</sup> for 4-methoxybenzamide;  $-1.93$ ,<sup>2</sup>  $-1.86$ ,<sup>5</sup> and  $-1.82$ ,<sup>4</sup> for 3,4,5-trimethoxybenzamide; and  $-2.35$ ,<sup>2</sup>  $-2.25$ ,<sup>5</sup> and  $-2.42$ ,<sup>4</sup> for 3-nitrobenzamide. The observed small variations in  $pK_{\text{BH}^+}$  with temperature (Table 2) are consistent with some protonation results for *N*-methylbenzamide in aqueous sulphuric acid at three temperatures.<sup>6</sup>

The  $H_A$  acidity function scale for aqueous perchloric acid at 298 K agrees closely (Table 3) with the scale determined by Yates *et al.*<sup>2</sup> The general trends in the variation of  $H_A$  with temperature are similar to the corresponding trends in the variation of  $H_0$  with temperature<sup>1</sup> although at high acid concentrations  $dH_A/dT$  is appreciably less than  $dH_0/dT$ .

The variation in  $\Delta H$  as a function of acid concentration for the three amides which have been studied gave as before<sup>1,7</sup> parallel curves in overlapping ranges of perchloric acid concentration. The parallelism confirms that values of  $\log_{10}(C_{\text{BH}^+}/C_{\text{B}})$  for the amide bases must be parallel functions of acid concentration not only at 298 K, in accord with the typical behaviour for series of related bases,<sup>3</sup> but also at all other temperatures in the range 288–318 K. Equation (iii)<sup>1,7</sup> is applicable for

$$\Delta H - \Delta H^0 = 2.303RT^2(dH_A/dT)_p \quad (\text{iii})$$

all the amides used to establish  $H_A$  as a function of temperature. Values (Table 6) of  $\Delta H - \Delta H^0$  at unit intervals of perchloric acid concentration were read off from a smooth curve drawn through the experimental data for the three amides which were studied. Calculations have been carried out to test whether the enthalpy data for the amide bases are in accord with

<sup>7</sup> R. H. Boyd and C.-H. Wang, *J. Amer. Chem. Soc.*, 1965, **87**, 430.

hydration theories of acidity function behaviour. Full details of the method of calculation and tabulations of

TABLE 6

Values of  $\Delta H - \Delta H^0$ ,  $n$ , and  $Q$  [equation (v)] calculated in relation to the assessment of the validity of equation (v)

$m_{\text{HClO}_4}$ mol kg <sup>-1</sup>	$\Delta H - \Delta H^0$ kJ mol <sup>-1</sup>	$n^a$	$Q^a$ kJ mol <sup>-1</sup>	$n^b$	$Q^b$ kJ mol <sup>-1</sup>
2	0.60	8.66	0.24	13.5	0.12
3	0.75	6.96	0.21	10.9	0.04
4	0.95	5.32	0.54	8.66	0.54
5	1.20	4.08	1.50	6.89	2.10
6	1.57	3.51	1.85	5.90	2.66
7	2.10	3.17	2.27	5.19	3.27
8	2.85	3.04	2.86	4.73	4.05
9	3.85	2.91	3.59	4.35	5.00
10	5.20	2.80	4.45	4.04	6.08
11	6.80	2.68	5.43	3.74	7.27
12	8.65	2.48	6.40	3.43	8.53
13	10.70	2.31	7.46	3.17	9.92
14	12.75	2.13	8.54	2.90	11.30

The number of water molecules  $n$  was calculated on the assumption that  $\log_{10}(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+})$  equals: <sup>a</sup>  $0.1\alpha C$ ; <sup>b</sup> 0.

the required data relevant to aqueous perchloric acid solutions have been given elsewhere.<sup>1</sup>

Values (Table 6) of  $n$ , the number of water molecules of hydration liberated when an amide molecule B combines with a proton to give  $\text{BH}^+$ , were deduced *via* equation (iv), in which  $\alpha$  is the fraction of perchloric

$$H_A = -\log_{10}(\alpha C) + n\log_{10}a_w - \log_{10}(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+}) \quad (\text{iv})$$

acid dissociated at concentration  $C$ ,  $a_w$  is the activity of water, and  $y_{\text{H}^+}$ ,  $y_{\text{B}}$ , and  $y_{\text{BH}^+}$  are the activity coefficients of  $\text{H}^+$ , B, and  $\text{BH}^+$ , respectively. Two separate sets of calculations were performed with the activity coefficient term  $\log_{10}(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+})$  in equation (iv) approximated as either equal to  $0.1\alpha C$  or equal to zero at all perchloric acid concentrations. The calculated values of  $n$  for the amide acidity function scale were subsequently used in the evaluation of the factor  $Q$  given by equation (v), in which

$$Q = -RT^2 (d \ln(\alpha\rho)/dT) - n\bar{L}_w \quad (\text{v})$$

$\rho$  is the density of a perchloric acid solution and  $\bar{L}_w$  is the relative partial molar enthalpy of water in that solution. Comparison of the values of  $Q$  (Table 6) with  $\Delta H - \Delta H^0$  as a function of perchloric acid concentration enabled an assessment to be made of the applic-

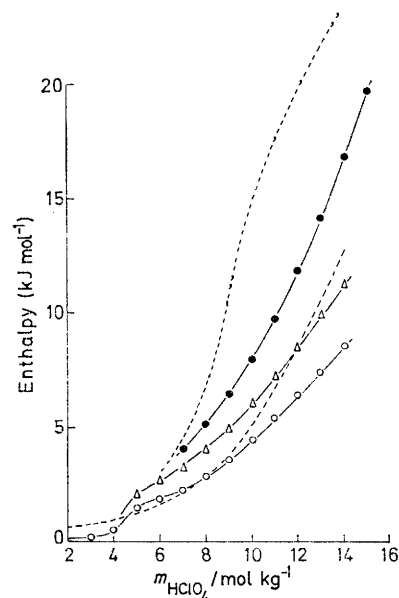
$$\Delta H - \Delta H^0 = RT^2 \frac{d \ln(\alpha\rho)}{dT} - n\bar{L}_w -$$

$$RT^2 \frac{d \ln(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+})}{dT} \quad (\text{vi})$$

ability of equation (vi) which follows<sup>1</sup> from differentiation of equation (iv) with respect to temperature.

The calculated values of  $Q$  and the  $\Delta H - \Delta H^0$  data are of the same sign and of approximately similar magnitude (Figure). The results therefore support the conclusion that the variation of  $\Delta H - \Delta H^0$  with

perchloric acid concentration is in accord with theories in which the variation of acidity functions with acid concentration is largely attributed to the release of water of hydration which occurs when a base B combines with a proton to give  $\text{BH}^+$ . Furthermore the observation that  $\Delta H - \Delta H^0$  for amides is less than for amines<sup>1</sup> at a particular acid concentration is consistent with the corresponding relationship between the calculated values of  $Q$  for the two classes of weak base (Figure). However the deviations between the experimental  $\Delta H - \Delta H^0$  values and between the calculated  $Q$  values for the amines and amides are not identical. The lack of quantitative agreement between the changes



Variation of  $Q$  with perchloric acid concentration. Curves for amide bases deduced *via* values of  $n$  calculated from equation (iv) with  $\log_{10}(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+})$  equal to  $\circ$   $0.1\alpha C$ ,  $\triangle$  zero. The lower dashed line is the experimental  $\Delta H - \Delta H^0$  curve for amides. The upper dashed curve represents the  $\Delta H - \Delta H^0$  data for primary amine bases and the points  $\bullet$  are the corresponding values of  $Q$  for amines calculated by taking  $\log_{10}(y_{\text{H}^+}y_{\text{B}}/y_{\text{BH}^+})$  equal to zero

in  $Q$  and  $\Delta H - \Delta H^0$  in passing from one structurally similar set of bases to another is hardly surprising in view of the assumptions which have been made in the present treatment with regard to the activity coefficient terms in equations (iv) and (vi). An exact correlation between experiment and the present simplified treatment would not be expected because of the specificity and complexity of the behaviour of activity coefficients for solute species in concentrated electrolyte solutions.<sup>2,8,9</sup>

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<sup>8</sup> T. R. Essig and J. A. Marinsky, *Canad. J. Chem.*, 1972, **50**, 2254.

<sup>9</sup> R. H. Boyd, 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, p. 97.