Thermochimica Acta, 103 (1986) 259–266
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYTICAL PROPERTIES OF THE AMIDOXIME GROUP. X. POTENTIOMETRIC AND THERMOMETRIC BEHAVIOUR OF 3,5-DIMETHYL-4-ISOXAZOLYLACETAMIDOXIME

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(Received 12 December 1985)

ABSTRACT

Dissociation equilibria of 3,5-dimethyl-4-isoxazolyl-acetamidoxime (DMIAA) were studied by means of potentiometric and thermometric techniques in ethanol–water media.

Refined pK values (p$K_1 = 4.05$; p$K_2 = 11.34$) and neutralization enthalpy ($\Delta H_1 = -7.57$ kcal mol^{-1}) were obtained using several computer programs (GRAN, MINIPOT, MINIQUAD and MINITERM).

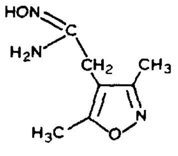
Titration errors and thermodynamic parameters of DMIAA are compared to the corresponding values obtained for other amidoximes studied in previous papers.

INTRODUCTION

Amidoximes are a group of analytical reagents with several interesting applications [1]. In a research project directed towards a better knowledge of this group, we studied the behaviour of different aliphatic amidoximes [2–6] and some in which the amidoxime group is supported by a hetero-ring [7].

So, in a previous paper [5] we prepared a new compound, DMIAA, and determined its solubility in different solvents, R_f values, IR, UV–Vis, mass, proton and C-13 NMR spectra, etc. The behaviour of DMIAA as analytical reagent was also studied, showing this compound to have several interesting reactions.

In order to gain a better understanding of this new reagent, in the present paper we study the thermodynamic behaviour of DMIAA using potentiometric and thermometric techniques.



DMIAA

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EXPERIMENTAL

Reagents

DMIAA was obtained from the corresponding dinitrile, as described elsewhere [5].

All the other reagents were of analytical grade and their solutions were prepared with bidistilled water.

Apparatus

A Philips potentiometer PW 9414 ion activity meter, with glass AG 9100 and calomel K401 Metrohm electrodes was used.

All solutions were adjusted to 0.1 M ionic strength with KCl in the potentiometric experiments. Hydrochloric acid was added to perform the calibration of the electrodes in situ. All titrations were carried out at $25.0 \pm 0.1°C$ and a stream of nitrogen was bubbled through the sample in order to homogenize and achieve an inert atmosphere. Due to the low solubility of DMIAA in water, an ethanol–water mixture (20% v/v) was used.

Apparatus and experimental conditions for thermometric measurements were the same as those described in previous papers [8]. In all cases, 50 ml of solution of the sample were titrated at 25°C.

For calculations, an experimental value of 0.0524 kcal $°C^{-1}$ for the initial heat capacity of the system was used, which was corrected for the effect of dilution during the titrations. Thermometric titrations were performed in a mixture of ethanol–water (50% v/v).

Calculations

A HP-85 Hewlett-Packard microcomputer was used for GRAN, MINIPOT and MINITERM. A Digital Vax/VMS 11 was used for MINIQUAD.

RESULTS

The data resulting from electrode calibrations were treated by the GRAN program [9], which allowed us to obtain several parameters in the current experimental conditions: standard potential of the glass electrode, ionic product of water, etc. The resulting values were used as starting parameters for the refinement program MINIPOT [10] which also gave us the junction potentials of the electrodes.

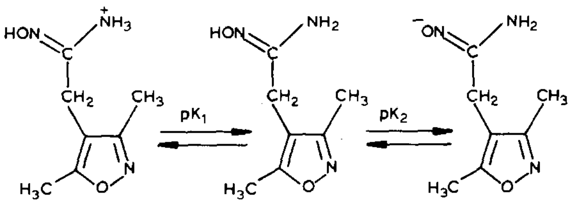
TABLE 1

pK values of DMIAA obtained by several methods ($E^0 = 360.6$ mV; p$K_w = 14.02$; $t = 25.0 \pm 0.1$°C; $I = 0.1$ M KCl; ethanol–water (20% v/v))

Method	pK_1	pK_2	U (E^{-6})	s (E^{-5})	pK_w	X^2	R
$\bar{j}$ plot	4.00	11.73	–	–	14.01		
MINIPOT	4.32	10.86	3.1458	9.042	14.05	37.75	0.03594
MINIQUAD	4.05	11.34	1.8390	7.269	14.05	52.41	0.02890

On the other hand, the potentiometric curves corresponding to the titrations of DMIAA in presence of HCl were used to calculate the values of $\bar{j}$ [11], which were represented versus pH to determine approximately the dissociation constant values. These constants were first refined simultaneously with the standard potential by means of the program MINIPOT, and then with MINIQUAD [12,13] which is a more powerful program but does not refine E^0.

The results show that DMIAA has two dissociation constants (Table 1), one for the protonation of the $-NH_2$ and the other for the deprotonation of the oxime group



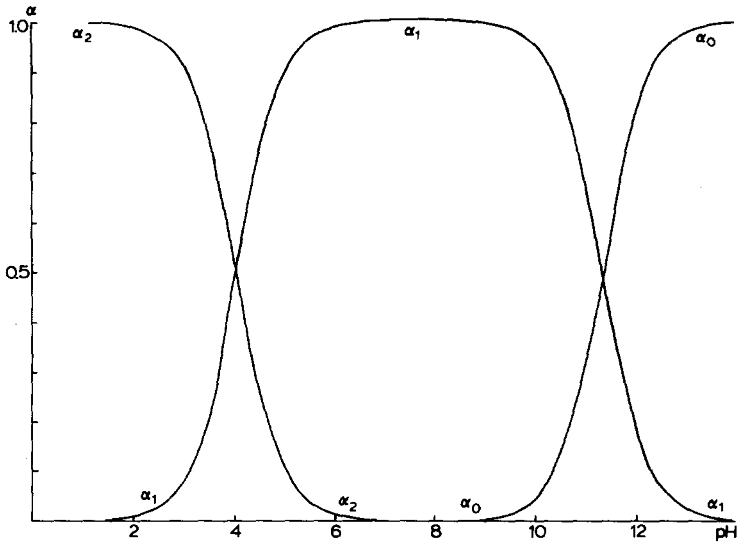


Fig. 1. Distribution diagram of DMIAA.

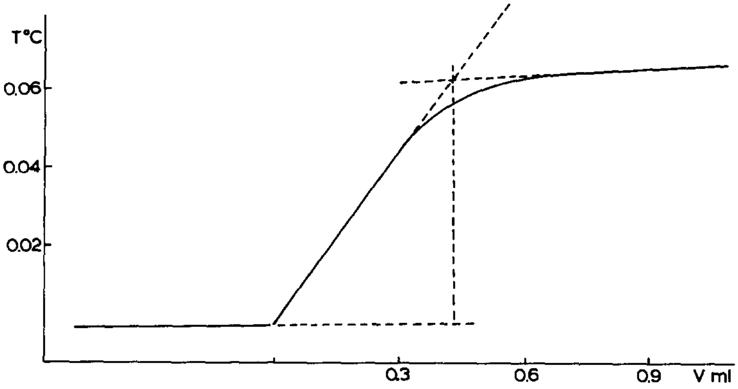


Fig. 2. Thermometric titration curve of DMIAA 1.1117 M with HCl 0.9834 M in an ethanol–water mixture (50% v/v).

In Fig. 1 the distribution diagram of DMIAA is presented.

A thermometric curve of DMIAA, obtained in ethanol–water (50% v/v) medium and using HCl 0.9834 N as titrant, is represented in Fig. 2.

Three independent samples of DMIAA were thermometrically titrated in order to obtain their corresponding errors.

Experiment	Concentration, M	% Error
1	8.1507 E−3	−4.68
2	1.1112 E−2	−4.97
3	8.5891 E−3	−2.65

The high errors are probably due to the unfavorable pK_b values of the NH_2 group of DMIAA.

In the determination of neutralization enthalpies of DMIAA, initially present in its electrically neutral form, two cases can be considered: (a) the nitrogen-containing groups are protonated with HCl, and (b) the oxime proton is neutralized with NaOH.

As was formerly shown [14], the high pK_a values of the oxime group prevent the titration of amidoximes with NaOH and renders impossible calculation of neutralization enthalpies of these groups.

Several independent methods were used to calculate the neutralization enthalpy of the $-NH_2$ group of DMIAA with HCl.

Overall heat capacity method

This consists of measuring the total temperature variation produced in the titration of n moles of the substance, supposing a complete reaction, and applying the equation

$$\Delta H = -Q/n = -c\,\Delta T/n$$

The following results were obtained

Experiment	n (mol, E−4)	ΔT(°C)	ΔH_n (kcal mol^{-1})
1	4.0754	0.0620	−7.98
2	4.5585	0.0624	−7.17
3	4.2945	0.0632	−7.71

Point-by-point heat capacity methods

These methods consist of analyzing point by point the thermometric titration curve. For each point, from the expression for the equilibrium constant and the charge, matter and heat balances, results

$$-K_a\ \Delta H = \frac{C_a C_b V_T}{Q_{T_i}} \Delta H^2 + (C_a + C_b)\ \Delta H + \frac{Q_{T_i}}{V_T} \tag{1}$$

Method 1

This was used by Christensen and coworkers [15] to calculate the value of ΔH and pK_a of bisulphate. Equation (1) may be represented in the form

$$-K_a\ \Delta H = A\ \Delta H^2 + B\ \Delta H + C$$

As the left-hand side remains constant throughout the titration curve, for any two points of the enthalpogram (i, j), the following is verified

$$(A_i - A_j)\ \Delta H^2 + (B_i - B_j)\ \Delta H + (C_i - C_j) = 0$$

which allows evaluation of ΔH, since A, B and C are calculated from the titration data.

The results obtained in three independent titrations of DMIAA are: Expt. 1: $\Delta H_N = -7.64$ kcal mol^{-1}; Expt. 2: $\Delta H_N = -7.83$ kcal mol^{-1}; Expt. 3: $\Delta H_N = -7.58$ kcal mol^{-1}.

Method 2

On rearranging eqn. (1), one obtains

$$\frac{C_0 T V_T}{C_b^0 V_0^2} = -\Delta H - \frac{C_0 T V_T}{C_b^0 V_0^2} \frac{K_a}{h}$$

which may be expressed in a simplified form as

$$B = -\Delta H - (B/h) K_a$$

(A more detailed discussion can be found in ref. 14.)

The results obtained by this method, with one of the thermometric titrations of DMIAA, are represented in Table 2.

TABLE 2

Determination of the neutralization enthalpy of $-NH_2$ group of DMIAA (method 2, experiment 2; $C_a^0 = 0.9834$ M; $C_b^0 = 0.0091$ M; $V_0 = 50$ ml; $pK = 4.05$; $C_0 = 0.0524$ kcal $°C^{-1}$) [a]

V_T	ΔT(°C)	pH	$X_i(E^4)$	Y_i
50.152	0.0220	4.375	5.889	2.482
50.190	0.0272	4.225	5.161	3.071
50.229	0.0332	4.086	4.578	3.751
50.267	0.0384	3.951	3.878	4.342
50.305	0.0430	3.813	3.178	4.889
50.343	0.0480	3.667	2.524	5.436
50.381	0.0536	3.506	1.950	6.075
50.419	0.0566	3.327	1.290	6.080

[a] $r = 0.9922$; $\Delta H = -7.47 \pm 0.40$ kcal mol^{-1}; $pK_a = 4.08 \pm 0.05$.

Method 3

Expression (1) may be reordered to give the final equation

$$\frac{V_0^2(C_a^0 - C_b^0) - V_0 V_T(K_a + C_a^0)}{C_0 V_T\, \Delta T} = \frac{C_a^0 C_b^0 V_0^3 (V_T - V_0)}{C_0^2 V_T^2\, \Delta T^2} \Delta H + \frac{1}{\Delta H}$$

which, as in the previous cases, allows the experimental data to be adjusted by means of the Gauss–Newton method to obtain the value of ΔH from either the intercept or the slope.

The results obtained by this method for the calculation of the neutralization enthalpy of DMIAA in one of the experiments are given in Table 3.

As may be observed, the values of ΔH obtained from the slope coincide perceptibly with those obtained from the intercept.

TABLE 3

Determination of the neutralization enthalpy of the $-NH_2$ group of DMIAA (method 3, expt: 2; $C_a^0 = 0.9834$ M; $C_b^0 = 0.0091$ M; $V_0 = 50$ ml; $pK_a = 4.05$; $C_0 = 0.0524$ kcal $°C^{-1}$) [a]

V_T	ΔT(°C)	$X_i(E^{-2})$	Y_i
50.192	0.0272	4.337	−0.462
50.231	0.0332	3.488	−0.400
50.269	0.0384	3.037	−0.364
50.308	0.0432	2.738	−0.340
50.346	0.0480	2.491	−0.321
50.385	0.0536	2.217	−0.300
50.423	0.0552	2.295	−0.305

[a] $r = -0.9998$; $\Delta H_N = -7.69 \pm 0.01$ kcal mol^{-1} (intercept); $\Delta H_N = -7.68 \pm 0.19$ kcal mol^{-1} (slope).

TABLE 4

Refinement of pK and ΔH values of 3,5-dimethyl-4-isoxazolylacetamidoxime with MINITERM: experiment 2; initial heat capacity 0.0524 kcal °C^{-1}; $T_L = 9.117(E^{-3})$ M; $T_M = 0$ [a]

V(ml)	pH	Tot. M	Tot. L(E^{-3})	$T_{meas.}$	T_{calc}	D
0.152	4.375	1.000	9.089	0.02200	0.02201	−0.00001
0.190	4.225	1.000	9.082	0.02720	0.02743	−0.00023
0.229	4.086	1.000	9.075	0.03320	0.03278	+0.00042
0.267	3.951	1.000	9.069	0.03840	0.03804	+0.00036
0.305	3.813	1.000	9.062	0.04300	0.04322	−0.00022
0.343	3.667	1.000	9.055	0.04800	0.04823	−0.00023
0.381	3.506	1.000	9.048	0.05360	0.05300	+0.00060
0.419	3.327	1.000	9.041	0.05660	0.05724	−0.00064

q	p	r	log β	ΔH (cal mol^{-1})
0.00	1.00	1.00	4.05	$-78.87\ E^{-2}$

[a] $\Delta H_M = 00.00$ E−1 cal mole^{-1}. $\Delta H_L = 00.00$ E−1 cal mole^{-1}. Square of residuals = 1.238 E−6. Standard deviation = 0.00050°C. Error of parameter no. 2 = 1.1649 E−2. Error of parameter no. 1 = 1.0158 E−2.

TABLE 5

Values of pK and ΔH of the amidoxime groups of DMIAA and other amidoximes

Compound	pK_1	pK_2	pK_3	pK_4	$-\Delta H_1$	$-\Delta H_2$	ΔH_3	ΔH_4	Reference
ODPA [c]	4.60 [a]	6.06 [a]	11.21 [b]	–	6.09 [a]	8.05 [a]	–	–	[3,14]
TDPA [d]	4.56 [a]	5.80 [a]	11.05 [b]	–	6.71 [a]	7.68 [a]	–	–	[3,14]
IDPA [e]	3.18 [a]	4.79 [a]	8.66	11.39 [b]	6.38 [a]	7.81 [a]	8.81	–	[3,14]
DMIAA [f]	4.05 [a]	11.34 [a]	–	–	7.57 [a]				This work
DMIA [g]	3.73 [a]	11.66 [a]	–	–	7.10 [a]				[7]
MPIA [h]	2.34 [a]	–	–	–					[7]
DPIA [i]	2.96 [a]	4.83 [a]	11.96 [b]	–					[7]

[a] $-NH_2$ group. [b] = NOH group. [c] ODPA = 3,3′-oxidipropidamidoxime. [d] TDPA = 3,3′-thiodipropidamidoxime. [e] IDPA = 3,3′-iminodipropidamidoxime. [f] DMIAA = 3,5-dimethyl-4-isoxazolylacetamidoxime. [g] DMIA = 3,5-dimethyl-4-isoxazolylamidoxime. [h] MPIA = 3-phenyl-5-methyl-4-isoxazolylamidoxime. [i] DPIA = 3,5-diphenyl-4-isoxazolylamidoxime.

Finally, we have used MINITERM to refine the pK and ΔH values of DMIAA [16]. In Table 4 the good agreement between calculated and measured temperatures after refinement is shown. In Table 5 it can be observed that pK and ΔH values of the amidoxime group of DMIAA are similar to those obtained for other amidoximes previously studied.

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