Thermochimica Acta, 98 (1986) 19–30
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ANALYTICAL PROPERTIES OF THE AMIDOXIME GROUP. VIII. SYNTHESIS, SPECTRAL PROPERTIES, POTENTIOMETRIC AND THERMOMETRIC BEHAVIOUR OF 3,5-DIMETHYL, 3-PHENYL-5-METHYL AND 3,5-DIPHENYL-4-ISOXAZOLYLAMIDOXIME

J.L. BERNAL and M. PEDRERO

Department of Analytical Chemistry, Faculty of Sciences, University of Valladolid, Valladolid (Spain)

V. CERDÁ and J. CANTALLOPS

Department of Analytical Chemistry, Faculty of Sciences, University of Baleares, Palma de Mallorca (Spain)

(Received 30 July 1985)

ABSTRACT

Three 4-isoxazolyl-3,5-disubstituted amidoximes have been obtained and several of their physicochemical properties have been studied. The pK_a values have been potentiometrically determined, with each amidoxime having two protonation constants, one for low pH values (pK_a 2.24–2.96), and one for high pH values (pK_a 11.55–12.06).

The thermometric behaviour of 3,5-dimethyl-4-isoxazolylamidoxime is studied in an ethanol/water mixture (50%, v/v) in order to evaluate the error in its thermometric titration with HCl and the corresponding neutralization enthalpy at 25°C.

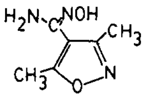
INTRODUCTION

The amidoximes are a group of analytical reagents which have offered several interesting applications [1].

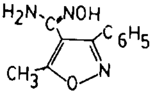
This group was mainly studied in the 50s by Kuras and Ruzicka [2,3]. In recent years, several papers dealing with analytical and physicochemical properties have appeared [4].

In a research project aiming to improve the knowledge of this group, we have obtained and studied the behaviour and analytical properties of several aliphatic amidoximes [5]. This paper initiates the study of a new group of reagents, in which the amidoxime group is supported by a hetero-ring. Three new compounds have been obtained, and several of their physicochemical properties determined.

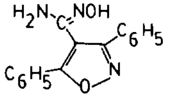
0040-6031/86/$03.50 © 1986 Elsevier Science Publishers B.V.



DMIA
(I)



MPIA
(II)

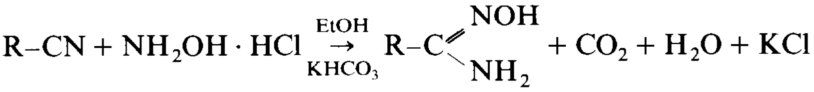


DPIA
(III)

EXPERIMENTAL

Synthesis

To obtain the isoxazolylamidoximes it was first necessary to prepare their corresponding nitriles. The amidoximes were obtained through the Thieman's method [5]:



$$R{-}CN + NH_2OH \cdot HCl \xrightarrow[KHCO_3]{EtOH} R{-}C\begin{array}{l}\nearrow NOH\\ \searrow NH_2\end{array} + CO_2 + H_2O + KCl$$

The nitriles, although of the same family, were prepared by different methods.

The 3,5-dimethylated compound (**I**) was obtained from ethylacetoacetate, through the diketone [6]. It was then cycled [7] into the functionalized isoxazol in position 4 with an ester group. Later this functional group was transformed to amide, which was dehydrated to nitrile.

The nitrile of the 3-phenyl-5-methylderivative (**II**) was achieved from 5-methylisoxazol [8] and chlorobenzaldoxime, which resulted from benzaldehyde.

Finally, in order to prepare 3,5-diphenylderivative (**III**) it was first necessary to obtain benzoylacetonitrile [9] from ethyl benzoate and chlorobenzaldoxime, which were cycled, as in the former synthesis.

Spectral behaviour

The IR spectra of the three compounds (which were obtained in KBr pellets), show the characteristic behaviour of this type of amidoxime [10,11].

The most important bands are included in Table 1. The structures deduced from the elucidation of the IR spectra, together with the results of the NMR (Table 2) and mass spectra, agree well with the expected compounds.

The UV–visible spectra of the 3,5-dimethyl and 3-phenyl-5-methyl amidoxime (both 10^{-4} M) were carried out in water, while for the 3,5-diphenyl derivative (10^{-5} M) a 50% (v/v) ethanol/water mixture was used (Figs. 1–3).

TABLE 1

Infrared spectra of the 3,5-disubstituted 4-isoxazolylamidoximes

	3,5-Dimethyl	3-Phenyl-5-methyl	3,5-Diphenyl
N–H asym. stretch	3610	3390	3400
O–H and N–H sym. stretch	3400–3100	3190	3320–3190
C–H stretch	2910	3050	3060
phenyl overtones	–	2000–1800	2000–1700
C=C, C=N stretch	1650	1660	1650–1630
N–H in-plane bending	1595	–	1570
=C–H in-plane bending	–	1450	1450–1420
$-CH_3$ asym. bending	1440	1440	–
=C–O, =C–N isoxazol stretch	1255–1105	1170–1100	1130–1030
N–OH stretch	945	900	950
phenyl ring bending	–	800–700	790–700
N–O bending	795	790	690

Determination of the ionization constants

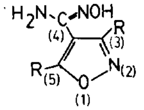
Ionization constants of the amidoximes were determined using the potentiometric method proposed by Gran [12,13].

The data resulting from the electrode calibrations were refined by MINIPOT [14], whereas those obtained in the titrations of the reagents were refined by MINIQUAD [15], both used successfully in previous papers [16].

All solutions were adjusted to 0.5 M ionic strength with KCl, and all titrations were performed at 25.0 ± 0.1°C. Nitrogen was bubbled through

TABLE 2

NMR spectra of the isoxazolylamidoximes:



	Ppm	Type	Assign.	No. H
3,5-Dimethyl-4-isoxazolylamidoxime	2.00	singlet	CH_3- (3)	3
	2.20	singlet	CH_3- (5)	3
	5.20	singlet	$-NH_2$	2
3-Phenyl-5-methyl-4-isoxazolylamidoxime	2.35	singlet	CH_3- (5)	3
	5.60	singlet	$-NH_2$	2
	7.40	multiplet	C_6H_5- (3)	5
	9.30	singlet	-OH	1
3,5-Diphenyl-4-isoxazolylamidoxime	7.67	multiplet	C_6H_5- (3,5)	10
	8.24	singlet	-OH	1

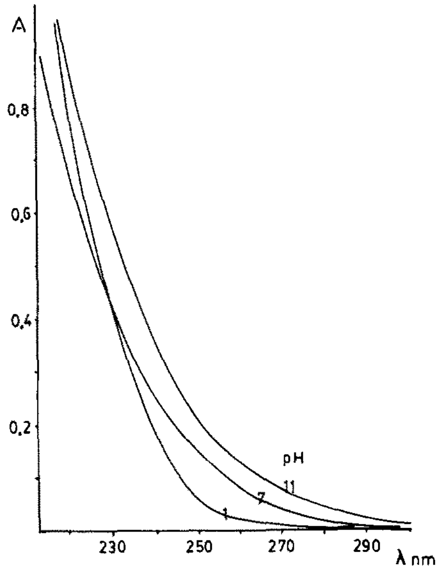


Fig. 1. Influence of pH on the UV–visible spectra of 3,5-dimethyl-4-isoxazolylamidoxime.

the solution in order to achieve an inert atmosphere and to homogenize the sample.

Apparatus

PW 9414 ion activity meter (Philips), with combined Metrohm AG 9100 electrode. Pye-Unicam spectrophotometer SP8-250 UV/vis. VAX/VMS 11 Digital computer.

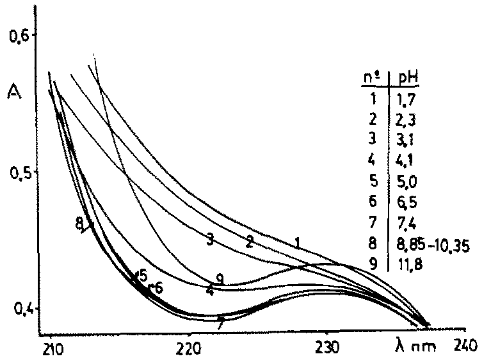


Fig. 2. Influence of pH on the UV–visible spectra of 3-phenyl-5-methyl-4-isoxazolylamidoxime.

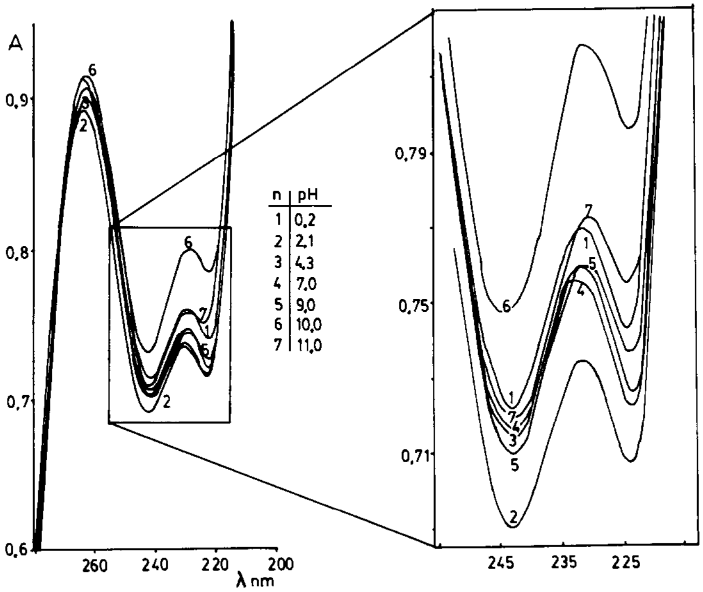


Fig. 3. Influence of pH on the UV–visible spectra of 3,5-diphenyl-4-isoxazolylamidoxime.

Reagents

All reagents were of analytical grade. The amidoximes were purified several times by recrystallization in hydroalcoholic mixtures, until constant melting point was attained (Table 3).

All solutions were prepared with deionized and bidistilled water, without CO_2.

Stock solutions

Stock solution of the 3,5-dimethyl derivative was prepared (5×10^{-3} M) in water ($I = 0.5$ M, KCl). Due to their low solubility in water (0.005 g/100 ml), the two other derivatives were prepared (10^{-3} M) in ethanol/water mixtures ($I = 0.5$ M, KCl); 20% (v/v) for the 3-phenyl-5-methyl derivative, and 50% (v/v) for the 3,5-diphenyl derivative.

Calculations

An HP-85 desk computer with 32k of RAM memory was used for MINIPOT. A Digital VAX VMS/11 was used for MINIQUAD.

TABLE 3

Melting points and elemental analyses of the isoxazolylamidoximes

Reagent	Melting point (°C)	Theoretical			Experimental		
		C	H	N	C	H	N
3,5-Dimethyl-4-isoxazolylamidoxime	142.5	46.45	5.81	27.10	46.24	5.83	25.34
3-Phenyl-5-methyl-4-isoxazolylamidoxime	155.0	60.83	5.07	19.35	60.43	5.10	20.70
3,5-Diphenyl-4-isoxazolylamidoxime	222.0	68.03	4.66	15.05	68.03	4.61	16.13

Thermometric behaviour

Due to the solubilities of the amidoximes, only the dimethyl-substituted compound could be thermometrically studied. To achieve the necessary solubility for thermometric titrations of this amidoxime an ethanol/water mixture (50%, v/v) had to be used.

The apparatus and experimental conditions were the same as those described previously [17].

In all cases, 50 ml of a solution of the sample were titrated at 25°C. It was not necessary to take into account the effect of the ionic strength, since it has been verified that this factor does not significantly influence the value of ΔH.

For the purposes of calculation, an experimental value of 0.0525 kcal $°C^{-1}$ for the initial heat capacity of the system was used, which was corrected for the effect of dilution during titration.

RESULTS

The potentials resulting from the titrations were mathematically treated by the Gran method [12,13] to determine several parameters, like the standard potential of the electrode and the value of the ionic product of water under the experimental conditions used. These parameters were refined with MINIPOT [14], which also allowed us to obtain the junction potentials of the electrodes (Table 4).

On the other hand, data resulting from the titration of the three reagents were used to calculate the values of $\bar{j}$ [18], which allowed us to determine approximate values of the dissociation constants when they were represented versus pH. Then these constants were refined by the program MINIQUAD [15].

The results showed that the isoxazolylamidoximes have two dissociation constants (Table 5), one for protonation of the amide group (low pH values) and the other for the deprotonation of the oxime group (high pH values).

Only for 3-phenyl-5-methyl-4-isoxazolylamidoxime have we not been able

TABLE 4

Electrode calibration values of the parameters obtained by means of the Gran and MINIPOT programs [12–14]

Medium	Method	pK_w	Log T_{OH}	E^0 (mV)	Log J_H	Log J_{OH}
water	Gran	13.686	−1.400	382.10	–	–
	MINIPOT	13.559	−1.400	376.73	2.144	3.350
ethanol/water	Gran	14.419	−1.134	382.79	–	–
(50%, v/v)	MINIPOT	14.409	−1.134	381.40	1.702	2.943

TABLE 5

Potentiometric dissociation constants of the isoxazolylamidoximes

Reagent	Method	
	$\bar{j}$ plot	MINIQUAD
3,5-Dimethyl-4-isoxazolylamidoxime	$pK_1 = 3.955 \pm 0.040$	$pK_1 = 3.734 \pm 0.054$
	$pK_2 = 11.548 \pm 0.121$	$pK_2 = 11.655 \pm 0.296$
	$pK_w = 13.559$	$pK_w = 13.764 \pm 0.014$
3-Phenyl-5-methyl-4-isoxazolylamidoxime ethanol/water (20%, v/v)	$pK_1 = 2.397 \pm 0.020$	$pK_1 = 2.341 \pm 0.056$
	$pK_w = 14.064$	$pK_w = 14.062 \pm 0.021$
3,5-Diphenyl-4-isoxazolylamidoxime ethanol/water (50%, v/v)	pK_1 2.326, 2.500	$pK_1 = 2.957 \pm 0.109$
	$pK_2 = 3.022 \pm 0.053$	$pK_2 = 4.826 \pm 0.074$
	$pK_3 = 12.096 \pm 0.346$	$pK_3 = 11.957 \pm 0.105$
	$pK_w = 14.409$	$pK_w = 14.396 \pm 0.001$

to determine the pK_a value of the oxime group, probably due to its very high value.

The dissociation constants for 3,5-diphenyl-4-isoxazolyl-amidoxime were obtained in ethanol/water medium (50%, v/v), and then extrapolated to aqueous medium [19]. For this compound there are two low dissociation constants which overlap. One of these constants does not appear in the other two compounds of the family.

The lowest pK value is decomposed in the other two compounds when $\bar{j}$ is used, but only one converges with MINIQUAD, the other is eliminated.

This different behaviour of this amidoxime with respect to the others may be due to the presence of two phenyl groups in the molecule [20,21].

The thermometric titration curve of the dimethyl compound obtained in an ethanol/water mixture (50%, v/v) using HCl (0.1933 M) as titrant is represented in Fig. 4.

The high pK_b value of the amidoxime justifies the final rounding of the enthalpogram, which explains the analytically unacceptable titration error of this compound ($\epsilon \approx 20\%$).

In the determination of neutralization enthalpies for the amidoxime initially present in electrically neutral form, two cases could be considered: (1) that in which the nitrogen-containing group is protonated with HCl, and (2) that in which the oxime proton is neutralized with NaOH. As has already been seen [22], the high pK_a values of the oxime groups prevent the titration of amidoximes with NaOH and render calculation of the neutralization enthalpies of these groups impossible.

Several independent methods were used to calculate the neutralization enthalpy of the amidoxime group with HCl.

Overall heat capacity method

This consists of measuring the total temperature variation produced in the titration of *n* moles of a substance, assuming complete reaction, and

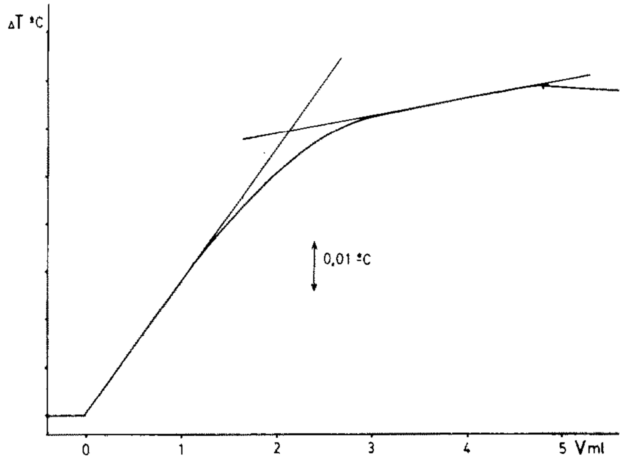


Fig. 4. Thermometric titration curve of 3,5-dimethyl-4-isoxazolylamidoxime (1.02×10^{-2} M in ethanol/water, 50%, v/v).

applying the equation:

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

The following results were obtained for 0.510 moles of the amidoxime.

Expt.	ΔT (°C)	ΔH_n (kcal mol^{-1})
1	0.0696	−7.16
2	0.0644	−6.54

Point-by-point heat capacity method

This method consists of analysing point-by-point the thermometric titration curve. For each point, from the expression for the equilibrium constant and the charge, matter and heat balances, we get:

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

(A more detailed discussion can be found in ref. 22.)

Method 1

This was used by Christensen et al. [23] 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, for any two points of the enthalpogram (i, j), it can be verified that:

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

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

The results obtained in two independent titrations of the dimethylisoxazolylamidoxime are:

Expt. 1: $\Delta H_{\mathrm{N}} = -7.69 \pm 0.33$ kcal mol^{-1}

Expt. 2: $\Delta H_{\mathrm{N}} = -7.54 \pm 0.28$ kcal mol^{-1}

Method 2

Rearranging eqn. (1), it is also found that:

$$\frac{C_0 T V_T}{C_{\mathrm{b}}^0 V_0^2} = -\Delta H - \frac{C_0 T V_T}{C_{\mathrm{b}}^0 V_0^2}\frac{K_{\mathrm{a}}}{h}$$

which may be expressed in a simplified form as:

$$B = -\Delta H + (B/h)K_{\mathrm{a}}$$

This expression is adjustable to the experimental values by means of the Gauss–Newton method. In order to apply this method, the value of the proton concentration h at each point must be known, either from a parallel potentiometric titration, or from calculus from a known K_{a} value. In the present case the pK_{a} value of the amide group is available, and therefore the second alternative was chosen.

The Brϕnsted equation was applied and the third degree equation was solved by means of the iterative method of Newton and Raphson. The results obtained by this method, with one of the thermometric titrations of the amidoxime, are presented in Table 6.

Method 3

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

$$\frac{V_0^2(C_{\mathrm{a}}^0 - C_{\mathrm{b}}^0) - V_0 V_T(K_{\mathrm{a}} + C_{\mathrm{a}}^0)}{C_0 V_T \Delta T} = \frac{C_{\mathrm{a}}^0 C_{\mathrm{b}}^0 V_0^3 (V_T - V_0)}{C_0^2 V_T^2 \Delta T^2}\Delta H + \frac{1}{\Delta H}$$

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. To apply this method of calculation it is first necessary to know the value of the acidity constant.

The results obtained by this method for the calculation of the neutralization enthalpy of the amidoxime in one of the experiments are given in Table 7. As may be appreciated, the values of ΔH obtained from the slope coincide perceptibly with those from the intercept.

TABLE 6

Determination of the neutralization enthalpy of the amide group of 3,5-dimethyl-4-isoxazolylamidoxime (method 2; experiment 2); $C_b^0 = 1.02E-2$ M; $C_a^0 = 1.933E-1$ M; $V_0 = 50$ ml; $pK_a = 4.03$; $C_0 = 0.0525$ kcal °C^{-1}

V_T (ml)	$T(°C; E^{-4})$	$h(E^{-5})$	$X_i(E^4)$	Y_i
0.491	130	1.730	6.628	1.147
0.614	164	2.267	6.389	1.450
0.695	184	2.654	6.141	1.630
0.818	220	3.284	5.947	1.953
0.900	240	3.743	5.703	2.134
1.023	272	4.495	5.395	2.425
1.104	292	5.045	5.168	2.607
1.227	324	5.956	4.869	2.900
1.309	348	6.628	4.706	3.120
1.432	376	7.753	4.358	3.379
1.513	394	8.593	4.127	3.546
1.636	424	10.01	3.820	3.825
1.718	440	11.09	3.586	3.976
1.841	468	12.93	3.278	4.239
1.922	482	14.35	3.048	4.372

$r = -0.9977$; $\Delta H = -7.235 \pm 0.184$ kcal mol^{-1}, $pK_a = 4.05$

TABLE 7

Determination of the neutralization enthalpy of the amide group of 3,5-dimethyl-4-isoxazolylamidoxime (method 3; experiment 2); $C_b^0 = 1.02E-2$ M; $C_a^0 = 1.933E-1$ M; $V_0 = 50$ ml; $pK_a = 4.03$; $C_0 = 0.0525$ kcal °C^{-1}

V_T (ml)	T (°C; $E-4$)	$X_i(E-2)$	Y_i
0.491	130	12.00	−1.01
0.614	164	9.383	−0.831
0.695	184	8.420	−0.755
0.818	220	6.896	−0.650
0.900	240	6.354	−0.607
1.023	272	5.594	−0.551
1.104	292	5.226	−0.522
1.227	324	4.693	−0.483
1.309	348	4.326	−0.458
1.432	376	4.034	−0.434
1.513	394	3.871	−0.421
1.636	424	3.596	−0.401
1.718	440	3.496	−0.392
1.841	468	3.295	−0.377
1.922	482	3.234	−0.372

$r = 0.9999$; $\Delta H_N = -7.29 \pm 0.00$ kcal mol^{-1} (intercept); $\Delta H_N = -7.37 \pm 0.06$ kcal mol^{-1} (slope)

TABLE 8

Refinement of p*K* and ΔH values of 3,5-dimethyl-4-isoxazolylamidoxime with MINITERM; experiment 2; initial heat capacity 0.0525 kcal °C^{-1}; $T_L = 0.01202$ M; $T_M = 0$

V (ml)	pH	Tot. M	Tot. L	T_{meas}	T_{calc}	*D*
0.491	4.762	1.000*E* +0	1.190*E* −2	0.01300	0.01332	−0.00032
0.614	4.645	1.000*E* +0	1.187*E* −2	0.01640	0.01656	−0.00016
0.695	4.576	1.000*E* +0	1.186*E* −2	0.01840	0.01871	−0.00031
0.818	4.484	1.000*E* +0	1.183*E* −2	0.02200	0.02187	0.00013
0.900	4.427	1.000*E* +0	1.181*E* −2	0.02400	0.02398	0.00002
1.023	4.347	1.000*E* +0	1.178*E* −2	0.02720	0.02711	0.00009
1.104	4.297	1.000*E* +0	1.176*E* −2	0.02920	0.02916	0.00004
1.227	4.225	1.000*E* +0	1.173*E* −2	0.03240	0.03221	0.00019
1.309	4.179	1.000*E* +0	1.171*E* −2	0.03480	0.03421	0.00059
1.432	4.111	1.000*E* +0	1.169*E* −2	0.03760	0.03719	0.00041
1.513	4.066	1.000*E* +0	1.167*E* −2	0.03940	0.03913	0.00027
1.636	3.999	1.000*E* +0	1.164*E* −2	0.04240	0.04207	0.00033
1.718	3.955	1.000*E* +0	1.162*E* −2	0.04400	0.04397	0.00003
1.841	3.888	1.000*E* +0	1.159*E* −2	0.04680	0.04681	−0.00001
1.922	3.843	1.000*E* +0	1.158*E* −2	0.04820	0.04867	−0.00047

q	*p*	*r*	Log β	ΔH (cal mol^{-1})
0.00	1.00	−1.00	4.0597	−70.950*E* +2

$\Delta H_M = 0.000E-1$ cal mol^{-1}
$\Delta H_L = 0.000E-1$ cal mol^{-1}
Square of residuals = 1.209*E* − 6°C^2
Standard deviation = 0.00032°C
Error of parameter No. 2 = 3.7487*E* + 1
Error of parameter No. 1 = 2.7169*E* − 3

We have used MINITERM to refine the p*K* and ΔH values of 3,5-dimethyl-4-isoxazolylamidoxime [24]. In this program the overall enthalpies and the logarithms of the overall stability constants are treated as unknown parameters, and the values which give the minimum of the non-weighted sum of squares of residuals of the measured and calculated temperature increments are calculated, together with the probable errors:

$$U(\log\beta_i, \Delta H_i) = \sum_i (\Delta T_{\mathrm{meas},i} - \Delta T_{\mathrm{calc},i})^2$$

$$= \sum_i \left(\Delta T_{\mathrm{meas},i} - \left(\Delta H_M[\mathrm{M}] - \Delta H_L[\mathrm{L}] - \sum_j \Delta H_j \beta_j [\mathrm{M}]^{qj} [\mathrm{L}]^{pj} \times [\mathrm{H}]^{rj} \right) V_0/C_0 \times 1000 \right)^2$$

In Table 8 the good agreement between the calculated and measured temperatures after refinement is shown.

TABLE 9

Thermodynamic values of 3.5-dimethyl-4-isoxazolylamidoxime calculated with the point-by-point heat capacity methods and MINITERM

Exp.	ΔH			MINITERM			
	Method 1	Method 2	Method 3	pK	ΔH	s	U
1	-7.69 ± 0.33	-7.68 ± 0.23 $\mathrm{p}K_a = 4.04$ $r = 0.9977$	-7.60 ± 0.05 $r = 0.9998$	4.049 ± 0.003	-7.57 ± 0.05	0.0004	$1.85E-6$
2	-7.54 ± 0.28	-7.23 ± 0.18 $\mathrm{p}K_a = 4.05$ $r = 0.9980$	-7.33 ± 0.06 $r = 0.9999$	4.059 ± 0.003	-7.10 ± 0.04	0.0003	$1.21E-6$

In Table 9 the values of U and s (standard deviation) can be seen, calculated with the point-by-point heat capacity methods and the same values after refinement with MINITERM.

REFERENCES

1 F. Eloy and R. Lenaers, Chem. Rev., 62 (1962) 155.
2 M. Kuras, Chem. Listy, 38 (1944) 54; 44 (1950) 41, 90; 45 (1951) 33; 46 (1952) 482; 48 (1954) 1275.
3 M. Kuras and E. Ruzicka, Chem. Listy, 47 (1953) 1870.
4 G.A. Pearse and R.T. Pflaum, J. Am. Chem. Soc., 81 (1959) 6505.
5 F. Thieman, Chem. Ber., 17 (1884) 126.
6 G. Renzi, V. Dal Piaz and S. Pinzati, Gazz. Chim. Ital., 98 (1969) 753.
7 U.P. Bow and S.P. Yahar, J. Chem. Soc., 23 (1946) 189.
8 H.A. Albrecht and J.T. Plati, Chem. Abstr., (1969), 70, 386, 68349w.
9 J. Long, J. Am. Chem. Soc., 69 (1947) 990.
10 C.L. Bell, C.N.V. Nambury and L. Bauer, J. Org. Chem., 29 (1969) 2873.
11 J. Barrans, R. Mathis-Noël and F. Mathis, C.R. Acad. Sci., 245 (1957) 419.
12 G. Gran, Acta Chem. Scand., 4 (1950) 559.
13 G. Gran, Analyst (London), 77 (1952) 661.
14 F. Gaizer and A. Puskas, Talanta, 28 (1981) 565.
15 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 53.
16 M.L. Albelda, V. Cerdá, R. Pardo and P. Sanchez-Batanero, Quim. Anal., 4 (1) (1983) 218.
17 V. Cerdá, E. Casassas, F. Borrull and M. Esteban, Thermochim. Acta, 55 (1982) 1.
18 J. Bjerrum (Ed.), Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen, 1941.
19 G. Charlot and B. Tremillon Les reactions chimiques dans les solvants et les sels fondus, Gauthier-Villars, Paris, 1963.
20 B. Lenarcik and M. Gabryszewski, Rocz. Chem., 52 (1978) 855.
21 J. Kuling and B. Lenarcik, Polish. J. Chem., 52 (1978) 477.
22 V. Cerdá, E. Casassas and F. Borrull Thermochim. Acta, 57 (1982) 195.
23 J.J. Christensen, R.M. Izatt, L.D. Hansen and J.A. Partridgen, J. Phys. Chem., 71 (1966) 2003.
24 V. Cerdá, J.M. Estela and R. Jara, Thermochim. Acta, 87 (1985) 13.