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ANALYTICAL PROPERTIES OF THE AMIDOOXIME GROUP. V. THERMOMETRIC STUDY OF 3,3′-OXY-, 3,3′-THIO- AND 3,3′-IMINODIPROPIOAMIDOOXIME

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ABSTRACT

The thermometric behaviour of three amidooximes (3,3′-oxy-, 3,3′-thio- and 3,3′-iminodipropioamidooxime) is studied in order to evaluate the errors in their thermometric titration with HCl and the corresponding neutralization enthalpies from the analysis of the enthalpograms. The dissociation parameters (ΔG_i, ΔH_i and ΔS_i) of the three compounds at 25°C are evaluated from the pK_a values and neutralization enthalpies.

INTRODUCTION

The amidooximes constitute a group of relatively little-known reagents, since, while some of their physico-chemical properties have been determined [1–5], their analytical properties have scarcely been studied. Because of this, and because they are intermediate products of imidooxime synthesis, which we have studied extensively [6–9], it seemed opportune to go deeper in order to gain a better understanding of their characteristics as well as to establish some of their analytical applications.

In an initial research project, the behaviour of α,α'-azobis(isobutiroamidooxime) was studied [10], and some specific tests for the identification of metallic ions were developed. The interest aroused by these results justified the study of other compounds with the diamidooxime group [11–14], with the result that some tests of analytical interest were obtained.

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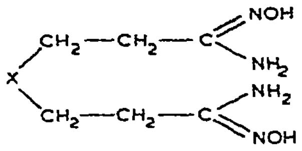
In the present paper, thermometric techniques are applied to the characterization of some of these compounds, specifically, 3,3′-iminobis(propioamidooxime), IDPA; 3,3′-oxybis(propioamidooxime), ODPA; and 3,3′-thiobis(propioamidooxime), TDPA:



IDPA, X = NH
ODPA, X = O
TDPA, X = S

EXPERIMENTAL

Thermometric apparatus

The apparatus and experimental conditions were the same as those described previously [15].

Reagents

The diamidooximes were obtained by reaction of the corresponding dinitriles with hydroxylamine [15,16].

Conditions of thermometric titrations

In all cases, 80 ml of a solution of the sample compound at 20°C were titrated. At the concentrations used, it was necessary to take into account the heat of dilution of the titrant, which was ascertained from the corresponding blank titration. It was not necessary to take into account the effect of the ionic strength, as it has been verified that this does not significantly influence the value of ΔH. For purposes of the calculations, an experimental value of 0.0893 kcal $°C^{-1}$ for the initial heat capacity of the system was used, which was corrected for the effect of dilution during the titrations.

Calculations

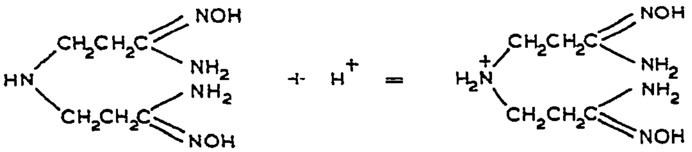
A Rockwell AIM 65 desk computer with 12 K of RAM memory was used for the calculations. The programs, in BASIC, together with the entry data and intermediate results are available on request.

RESULTS AND DISCUSSION

Titration curves and errors

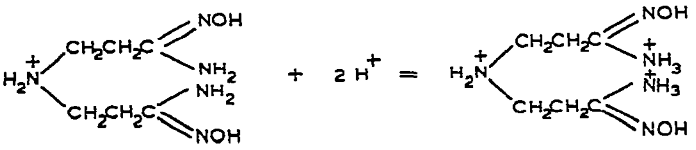
The titration curve of IDPA with HCl (Fig. 1) presents a clearly different aspect from that of the other two amidooximes, since in IDPA, an initial change of slope can be seen after the consumption of an equivalent of HCl per mole of IDPA. The titration curve ends, nevertheless, in a form analogous to that of the other two diamidooximes, with the simultaneous consumption of two more equivalents of HCl per mole of compound titrated.

These results are in complete agreement with those from potentiometric titrations [14], and can be interpreted easily as a function of the found values of pK_a. Thus, the different behaviour of the IDPA with respect to the two diamidooximes can be explained assuming that the protonation of the imine group (absent in ODPA and TDPA) occurs in the first place, since its pK_b value is lower than that of the two amidooxime groups present in the molecule:



$pK_{a3} = 8.47 \pm 0.03$

The higher, and similar, values of pK_b of the two amidooxime groups justify their simultaneous titration and the rounding of the curve about the second equivalence point



$pK_{a1} = 3.54 \pm 0.01$

$pK_{a2} = 4.58 \pm 0.01$

This final rounding of the enthalpogram requires obtaining the second equivalence point of IDPA by linear extrapolation of the titration curve, which explains why in this case a greater titration error would be obtained with respect to that obtained at the first equivalence point.

The absence of the imine group in the other two amidooximes justifies the simultaneous consumption of only two equivalents of HCl (ODPA: pK_{a1} = 4.61 ± 0.02 and pK_{a2} = 5.83 ± 0.02; TDPA: pK_{a1} = 4.95 ± 0.01 and pK_{a2} = 5.89 ± 0.02). Since the K_b values of these substances are lower than those of IDPA, a greater rounding of the second equivalence point of the enthalpogram for this latter compound is not surprising. The titration errors of the three amidooximes obtained by analyzing several independent samples of

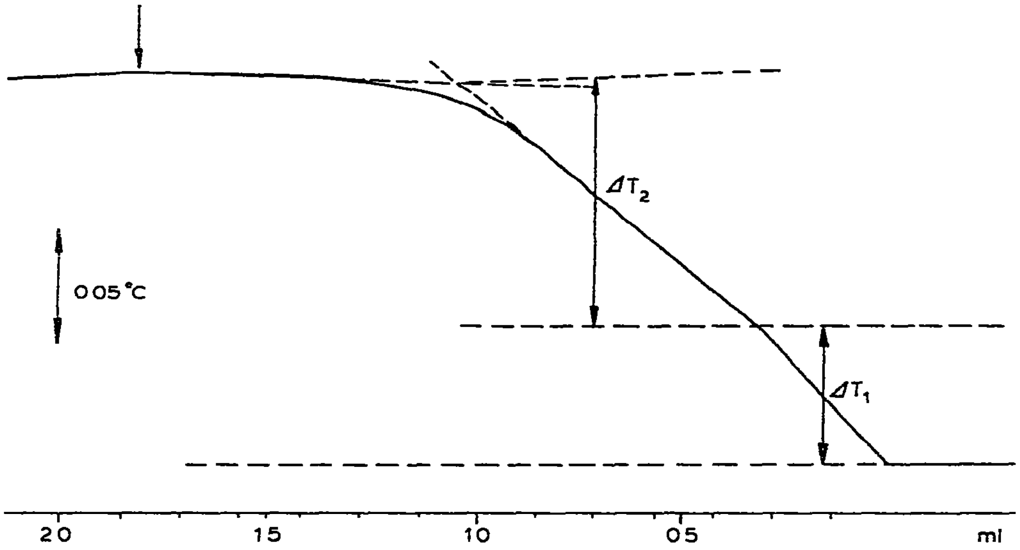


Fig 1. Calculation of the neutralization enthalpy of 1.0704×10^{-2} M IDPA with 1.9124 M HCl

each are given in Table 1. In each case, 1.9124 M HCl was used as titrant.

Titration of the two oxime groups with NaOH was also attempted. However, given their high pK_a values (greater than 11), these attempts proved unsuccessful. An attempt was also made to use the catalimetric titration method proposed by Vaughan and Swithenbank [17], based on the heat released in the polymerization of the acetone used as solvent. Nevertheless, because of the low solubility of the three amidooximes in acetone, these experiments were unsatisfactory.

Neutralization enthalpies

In the determination of neutralization enthalpies for amidooximes initially present in their electrically neutral forms, two cases could be considered: (1) that in which the nitrogen-containing groups are protonated with HCl, and (2) that in which the oxime protons are neutralized with NaOH. As has already been seen, the high pK_a values of the oxime groups prevent the titration of amidooximes with NaOH and renders calculation of the neutralization enthalpies of these groups impossible.

Neutralization enthalpy of the imine group of IDPA

Overall heat capacity method. This derives from the classic calorimetric method and consists of measuring the total temperature variation produced in the titration of n moles of a substance, supposing a complete reaction, and

TABLE I

Titration errors of the three amidooximes with HCl

Expt.	ODPA		TDPA		IDPA		
	Concn. (M)	E(2)	Concn. (M)	E(2)	Concn. (M)	E(1)	E(2)
1	6.5664×10^{-3}	1.42%	9.1827×10^{-3}	2.03%	8.9756×10^{-3}	0.82%	0.86%
2	7.9336×10^{-3}	1.81%	9.9949×10^{-3}	1.87%	1.0704×10^{-2}	0.62%	1.23%
3	9.6163×10^{-3}	1.40%	1.0419×10^{-2}	2.70%	1.1111×10^{-2}	0.55%	1.02%
			1.1256×10^{-2}	1.92%			
		$\bar{E}=\overline{1.54\%}$		$\overline{2.13\%}$		$\overline{0.66\%}$	$\overline{1.04\%}$

(1) Titration corresponding to the consumption of 1 equivalent of HCl/mole.

(2) Titration corresponding to the consumption of 2 equivalents of HCl/mole.

applying the equation [15]

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

As may be observed in Fig. 1, in the titration of the imine group of IDPA a linear zone is initially obtained, which shows that the basicity constant is favourable for thermometry. Since the slope of this zone is also steeper than that of the zone corresponding to the protonation of the two amidooxime groups, it is possible to apply the overall heat capacity method (Fig. 1), with which the following results are obtained

Expt	ΔT(°C)	n(moles)	ΔH_N(kcal mole^{-1})
1	7.00×10^{-2}	7.1805×10^{-4}	-8.72
2	8.10×10^{-2}	8.5632×10^{-4}	-8.46
3	8.41×10^{-2}	8.8880×10^{-4}	-8.46
			$\Delta \overline{H}_N = -8.55\pm 0.15$

Point-by-point heat capacity method This method consists 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

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

where, for the i point considered

$$Q_{T_i} = c\,\Delta T_i = (C_0 + V_i C_e \rho)\Delta T_i$$

$$c_a = \frac{c_a^0 V_i}{V_T}$$

and

$$c_b = \frac{c_b^0 V_0}{V_T}$$

where, c_a^0 = concentration of the titrant; c_b^0 = initial concentration of IDPA; V_i = volume of added titrant; V_0 = initial volume of IDPA; $V_T = V_0 + V_i$; Q_{T_i} = heat liberated by adding V_i; C_0 = initial heat capacity of the system; C_e = specific heat of the titrand; and ρ = density of the solution to be titrated.

Method A

This was used by Christensen et al. [18] 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 will 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 three independent titrations of IDPA are

Expt. 1: $\Delta H_N = -8.35 \pm 0.15$ kcal mole^{-1}

Expt. 2: $\Delta H_N = -8.37 \pm 0.39$ kcal mole^{-1}

Expt. 3: $\Delta H_N = -8.68 \pm 0.39$ kcal mole^{-1}

from which an average value of $\Delta \overline{H}_N = -8.47 \pm 0.31$ kcal mole^{-1} is derived.

Method B

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

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

which may be expressed in a simplified form as

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

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 (which permits the simultaneous calculation of ΔH and pK_a), 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 imine group is available [14], and therefore the second alternative was chosen. The Brønsted equation was applied and the third-grade 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 IDPA, are presented in Table 2.

Method C

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

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

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.

TABLE 2

Determination of the neutralization enthalpy of the imine group of IDPA (method B; experiment 2; $c_b^0 = 1.0704E-2$M; $c_a^0 = 1.9125$ M; $V_0 = 80$ ml; $pK_a = 8.47$; $C_0 = 0.0893$ kcal °C^{-1})

V_T(lit)	ΔT(°C)	h	X_i	Y_i
8.0107×10^{-2}	1.9400×10^{-2}	1.1500×10^{-9}	1.7600×10^{9}	2.0255
8.0143×10^{-2}	2.5600×10^{-2}	1.7000×10^{-9}	1.5700×10^{9}	2.6800
8.0178×10^{-2}	3.1900×10^{-2}	2.4100×10^{-9}	1.3800×10^{9}	3.3352
8.0214×10^{-2}	3.8700×10^{-2}	3.3300×10^{-9}	1.2200×10^{9}	4.0563
8.0250×10^{-2}	$4\ 5600\times10^{-2}$	4.5900×10^{-9}	1.0400×10^{9}	4.7781
$8\ 0286\times10^{-2}$	5.2500×10^{-2}	6.4000×10^{-9}	8.5900×10^{8}	5.5006
8.0321×10^{-2}	5.9400×10^{-2}	9.2300×10^{-9}	6.7400×10^{8}	6.2236
8.0357×10^{-2}	6.5000×10^{-2}	1.4200×10^{-8}	4.8000×10^{8}	6.8163
8.0393×10^{-2}	$7\ 3100\times10^{-2}$	$2\ 5900\times10^{-8}$	2.9600×10^{8}	7.6717
$r = 0.9996$	$\Delta H = -8.78\pm0.05$ kcal mole^{-1}		$pK_a = 8.41\pm0.01$	

The results obtained by this method for the calculation of the neutralization enthalpy of the imine group of IDPA in one of the experiments are given in Table 3. As may be appreciated, 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 imine group of IDPA (method C; experiment 2, $c_b^0 = 1.0704E-2$ M; $c_a^0 = 1.9125$ M; $V_0 = 80$ ml; $pK_a = 8\ 47$; $C_0 = 0.0893$ kcal mole^{-1})

V_T(lit.)	ΔT(°C)	X_i	Y_i
$8\ 0107\times10^{-2}$	1.9375×10^{-2}	$5\ 8305\times10^{-2}$	0 6118
8.0143×10^{-2}	2.5625×10^{-2}	$4\ 4403\times10^{-2}$	0.4921
$8\ 0178\times10^{-2}$	3.1875×10^{-2}	$3\ 5839\times10^{-2}$	0.4194
$8\ 0214\times10^{-2}$	3.8750×10^{-2}	$2\ 9075\times10^{-2}$	0 3675
8.0250×10^{-2}	4.5625×10^{-2}	$2\ 4446\times10^{-2}$	0 3261
$8\ 0286\times10^{-2}$	5.2500×10^{-2}	2.1082×10^{-2}	0.2977
$8\ 0321\times10^{-2}$	$5\ 9375\times10^{-2}$	1.8526×10^{-2}	0.2760
$8\ 0357\times10^{-2}$	6.5000×10^{-2}	1.7161×10^{-2}	0 2637
8.0393×10^{-2}	$7\ 3125\times10^{-2}$	1.4902×10^{-2}	0.2467
$r = 0.9999$	$\Delta H_N = -8\ 40\pm0.07$ kcal mole^{-1} (slope) $\Delta H_N = -8.32\pm0.002$ kcal mole^{-1} (intercept)		

Neutralization enthalpies of the amidooxime groups

Overall heat capacity method. The value of $\Delta H_T = \Delta H_1 + \Delta H_2$ of the amidooximes can be determined by applying the overall heat capacity method described for the protonation of the imine group of IDPA. Table 4 presents the results obtained by applying this method to the data derived from the titration of several independent samples of each of the three amidooximes considered.

Point-by-point heat capacity method. As the values of pK_{a1} and pK_{a2} of the two amidooxime groups are very close, it was necessary to calculate simultaneously the corresponding neutralization enthalpies. From the expressions for the equilibrium constants and the balances of matter, charge and heat, the final expression is deduced

$$-\frac{C_0 V_T \Delta T}{K_1 c_b^0 V_0^2 h}\left(h^2 + K_1 h + K_1 K_2\right) = \Delta H_2 + \Delta H_T \frac{h}{K_1} \tag{3}$$

which can be assimilated into a linear equation, and where the value of the

TABLE 4

Determination of ΔH_T of neutralization of the three amidooximes with HCl by means of the overall heat capacity method

Expt.	ΔT(°C)	n(moles)	$-\Delta H$(kcal mole^{-1})
IDPA			
1	1.0625×10^{-1}	7.1805×10^{-4}	13.21
2	1.2776×10^{-1}	8.5632×10^{-4}	13.32
3	1.3001×10^{-1}	8.8888×10^{-4}	13.07
			$\Delta \bar{H}_T = -13.20\pm0.12$
ODPA			
1	8.3530×10^{-2}	5.2531×10^{-4}	14.20
2	1.0000×10^{-1}	6.3469×10^{-4}	14.07
3	1.2336×10^{-1}	7.6930×10^{-4}	14.32
			$\Delta \bar{H}_T = -14.20\pm0.12$
TDPA			
1	1.1750×10^{-1}	7.3462×10^{-4}	14.28
2	1.2688×10^{-1}	7.9959×10^{-4}	14.17
3	1.3375×10^{-1}	8.3352×10^{-4}	14.32
4	1.4329×10^{-1}	9.0045×10^{-4}	14.21
			$\Delta H_T = -14.24\pm0.07$

proton concentration h may be calculated by applying the iterative method of Newton and Raphson to the equation

$$h^4 + \left(\frac{c_a^0 V_0}{V_T} - c_a^0 + \frac{2c_b^0 V_0}{V_T} + K_1 \right) h^3 + \left(\frac{c_a^0 V_0 K_1}{V_T} - c_a^0 K_1 + \right.$$
$$\left. + \frac{c_b^0 V_0 K_1}{V_T} + K_1 K_2 - K_w \right) h^2 + \left(\frac{c_a^0 V_0 K_1 K_2}{V_T} - c_a^0 K_1 K_2 - K_1 K_w \right) h -$$
$$- K_1 K_2 K_w = 0$$

In this way, the only unknowns in eqn. (3) are ΔH_2 and ΔH_T, whose values can be found by applying the least squares method. The results obtained by applying this method to the experimental values obtained in a titration of TDPA are shown in Table 5.

Calculation of the values ΔG_t, ΔH_t and ΔS_t of the amidooximes

Table 6 shows all the neutralization enthalpies of the three amidooximes obtained according to the several methods considered here. Once these values and those of pK_a of the three compounds are known [14], their thermodynamic ionization parameters may be easily calculated. For this it is

TABLE 5

Simultaneous determination of ΔH_1 and ΔH_2 of neutralization of TDPA (experiment 4; $c_b^0 = 1.1256E-2$ M; $c_a^0 = 1.9125$ M; $V_0 = 80$ ml; p$K_{a1} = 4.95$; p$K_{a2} = 5.89$)

V_T(lit)	ΔT(°C)	h	X_t	Y_t
8.0071×10^{-2}	1.06×10^{-2}	2.16×10^{-7}	1.88×10^{-2}	7.22
8.0143×10^{-2}	2.19×10^{-2}	4.96×10^{-7}	4.32×10^{-2}	7.79
8.0214×10^{-2}	3.34×10^{-2}	8.65×10^{-7}	7.54×10^{-2}	8.42
8.0286×10^{-2}	4.50×10^{-2}	1.36×10^{-6}	1.19×10^{-1}	9.15
8.0357×10^{-2}	5.56×10^{-2}	2.05×10^{-6}	1.79×10^{-1}	9.94
8.0428×10^{-2}	6.75×10^{-2}	3.03×10^{-6}	2.63×10^{-1}	11.3
8.0500×10^{-2}	7.87×10^{-2}	4.43×10^{-6}	3.86×10^{-1}	13.1
8.0571×10^{-2}	9.00×10^{-2}	6.52×10^{-6}	5.67×10^{-1}	15.8
8.0643×10^{-2}	1.00×10^{-1}	9.75×10^{-6}	8.49×10^{-1}	19.8
8.0714×10^{-2}	1.10×10^{-1}	1.52×10^{-5}	1.32	26.5
8.0785×10^{-2}	1.20×10^{-1}	2.57×10^{-5}	2.24	39.5
8.0857×10^{-2}	1.29×10^{-1}	5.32×10^{-5}	4.64	73.5

$r = 0.9999$ $\Delta H_1 = -7.43 \pm 0.13$ kcal mole^{-1}
$\Delta H_T = -14.28 \pm 0.12$ kcal mole^{-1}

TABLE 6

Neutralization enthalpies of the amidoximes with HCl

Compound	Method	Expt.	$-\Delta H_1$ (kcal mole^{-1})	$-\Delta H_T$(kcal mole^{-1})	$-\Delta H_3$(Kcal mole^{-1})	
IDPA	Overall	1		13.21		
		2		13.32		
		3		13.07		
	Point-by-p	1	7.22±0.29	13.42±0.51		
		2	6.96±0.31	13.25±0.19		
		3	7.09±0.53	12.66±0.33		
	Point-by-p (Method A)	1			8.35±0.15	
		2			8.37±0.39	
		3			8.68±0.39	
	(Method B)	1			8 65±0.08	
		2			8.78±0.05	
		3			8.55±0 12	
	(Method C)	1			8.44±0 06	
		2			8.40±0.07	
		3			8.46±0.09	
	Overall	1			8 72	
		2			8 46	
		3			8.46	
			$\overline{\Delta H_1} = -7.09\pm0.13$	$\Delta H_T = -13.16\pm0.27$	$\Delta H_3 = -8.53\pm0.14$	$\Delta H_2 = -6.07\pm0\ 28$
ODPA	Overall	1		14.20		
		2		14.07		
		3		14.32		
	Point-by-p	1	7.64±0.44	14.76±0.38		
		2	7.85±0.32	14.27±0 30		
		3	7.84±0.36	13.96±0.27		
			$\overline{\Delta H_1} = -7.78\pm0.12$	$\Delta H_T = -14\ 10\pm0.21$	$\Delta H_2 = -6.49\pm0.31$	

TABLE 6 (continued)

Compound	Method	Expt.	$-\Delta H_1$ (kcal mole^{-1})	$-\Delta H_T$(kcal mole^{-1})	$-\Delta H_3$(Kcal mole^{-1})
TDPA	Overall	1		14.28	
		2		14.17	
		3		14.32	
		4		14.21	
	Point-b-p	1	7.37±0.22	14.73±0.19	
		2	7.43±0.05	14.70±0.29	
		3	7.35±0.29	14.80±0.26	
		4	7.43±0.13	14.28±0.12	
			$\Delta H_1 = -7.40 \pm 0.04$	$\Delta H_T = -14.44 \pm 0.26$	$\Delta H_2 = -7.05 \pm 0.16$

TABLE 7

Values of ΔG_i, ΔH_i and ΔS_i of the studied compounds [a]

Compound	pK_1	ΔG_1	ΔH_1	ΔS_1	pK_2	ΔG_2	ΔH_2	ΔS_2	pK_3	ΔG_3	ΔH_3	ΔS_3
IDPA	3.54	4.83	7.17	7.85	4.58	6.25	6.15	−0.34	8.47	11.56	8.61	−9.8
ODPA	4.61	6.29	7.86	5.27	5.83	7.95	6.57	−4.63				
TDPA	4.95	6.75	7.48	2.45	5.89	8.04	7.13	−3.05				

[a] ΔG_i and ΔH_i in kcal mole^{-1}, ΔS_i in cal K^{-1} mole^{-1}.

sufficient to consider the expression

$$\Delta G_i = -RT \ln K_a$$

and to take into account the fact that the ionization enthalpies of the nitrogenated bases coincide with those of their neutralization enthalpies with changed sign. The entropy may be estimated by means of the expression

$$\Delta S_i = (\Delta H_i - \Delta G_i)/T$$

To calculate these values at 25°C it was necessary to correct those of the neutralization enthalpies, since they were determined at 20°C. For this, an averaged value of the molar heat capacity was used, deduced from the behaviour of several amines [18–20]. The values of the thermodynamic parameters of ionization of the three amidooximes at 25°C are given in Table 7.

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