CALORIMETRIC AND POTENTIOMETRIC STUDY OF THE DEPROTONATION REACTIONS OF VIOLURIC ACIDS

JOSÉ M. MORATAL*, ARACELI PRADES, MIGUEL JULVE and JUAN FAUS

Departamento de Química Inorgánica, Facultad de Química de la Universidad de Valencia, Burjassot (Valencia) (Spain)

(Received 18 January 1985)

ABSTRACT

Thermodynamic functions $\Delta G^{0\prime}$, $\Delta H^{0\prime}$ and $\Delta S^{0\prime}$ (25°C, 0.1 M KNO_3) of the deprotonation reactions of violuric, H_3V, methylvioluric, H_2MeV, and dimethylvioluric, HMe_2V, acids are determined. Both the enthalpy ($\Delta H^{0\prime} > 0$) and the entropy variations ($\Delta S^{0\prime} < 0$) contribute to the observed weak acid behaviour of these compounds. Trends in the $\Delta H^{0\prime}$ and $\Delta S^{0\prime}$ values are opposite and it is the latter which drives the pK_a sequence: $H_3V < H_2MeV < HMe_2V$. Thus, the "inductive effect" of methyl groups is an entropy, and not enthalpy, effect.

INTRODUCTION

Violuric acids are the 5-isonitroso derivates of barbituric acid (Fig. 1). They have been used in analytical chemistry for the identification and determination of metal ions, as developers in paper and thin-layer chromatography [1,2], as precipitation reagents, and particularly in colorimetry [3,4].

In recent years, some metal complexes of violuric acids with transition metal ions have been studied [5]. Violurate anions are coordinated to the metal ions, as bidentate ligands, through the nitrogen atom of the oxime group and an oxygen atom from a vicinal carbonyl group. These ligands are very interesting because of their π-acceptor properties. They have empty, low-energy π^* orbitals appropriate for back bonding and, thus, they are strong field ligands [6]. Recently, metal complexes of violuric acids have aroused some interest as model compounds of ferroverdin, a singular iron(II) siderophore [7].

Stability constants of some of these complexes have been determined [8], but there is a lack of the corresponding values of the formation enthalpies in spite of their interest. A complete thermodynamic characterization of the

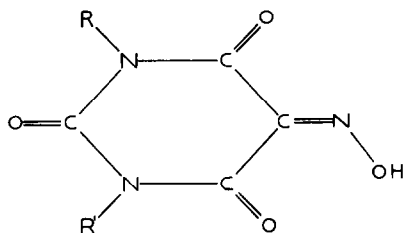---

* To whom correspondence should be addressed.

Fig. 1. Violuric acids: R=R′=H (violuric acid); R=Me; R′=H (methylvioluric acid); R=R′=Me (dimethylvioluric acid).

violurato complexes requires a previous knowledge of the ionization enthalpies of the violuric acids. As far as we know, the very scarce values of these enthalpies reported to date have been determined indirectly, from the temperature variation of the acidity constants [9,10].

In this work, we report a complete thermodynamic study of the deprotonation equilibria of violuric, methylvioluric and dimethylvioluric acids, directly determining the ionization enthalpies by flow microcalorimetry.

EXPERIMENTAL AND PROCEDURE

Reagents

Violuric acids were synthesized following the reported procedures [8,11,12]. All the other chemicals were Scharlau reagents.

Carbonate-free potassium hydroxide (0.1 M) and nitric acid ($(1–2.5) \times 10^{-3}$ M) solutions were used in the potentiometric and calorimetric studies.

Physical techniques

Potential measurements were performed with a Radiometer 84 pH-meter using a GK 2401C combined glass electrode. Dry O_2-free N_2 saturated with water vapour was bubbled through the solution in the reaction vessel. Measurements were made at $25.0 \pm 0.1°C$ and 0.1 M KNO_3. The concentration of hydrogen ion was calculated from the experimental EMF values, E (expressed in mV), by means of the expression

$$[H^+] = \exp{(E - E^{0\prime})/25.692}$$

The experimental values of the EMF have not been corrected for the liquid junction potential or for the potential drift of the electrode during the measurements. Preliminary acid–base titrations which were carried out under the same experimental conditions showed that the corrections due to the above effects were negligible over the pH range investigated. The electrode

was always calibrated as a hydrogen ion concentration probe, but, as a matter of convenience, pH instead of $-\log[H^+]$ is used throughout the text. Accurate concentration values of the basic titrant, as well as the $E^{0\prime}$ value, were determined with an aqueous nitric acid solution, which was previously standardized, before each titration series. The ionic product of water was determined under the same experimental conditions. The value found ($pK_w = 13.77$) is in good agreement with those previously reported [13]. On the other hand, we have used the experimental techniques and the data treatment which are generally recommended [14].

Calorimetric measurements were carried out with an LKB 10700-1 flow microcalorimeter, using a "mixing cell". The thermostat of the calorimeter was maintained at 25.00°C. Water at 18.00 ± 0.05°C was passed through the cooling coils of the air-bath and room temperature was kept at 22.5 ± 1°C. Reagent solutions were pumped through the calorimeter by two LKB 2132 MicroPerspex peristaltic pumps. The pumps were frequently calibrated by weighing the amount of water pumped in a known amount of time. The detector sensitivity was 0.062 $\mu V/\mu W$ and the calibration current had an accuracy of $\pm 0.1\%$. The thermal output was amplified by a Keithley 150B microvolt amplifier and recorded on a potentiometric recorder. The calorimetric measurements were performed as follows: the baseline output potential was taken when solution 1 (that is, the solution of the corresponding violuric acid which was partially neutralized) and solution 2 (ionic medium) were pumped through the cell. When a stable baseline was obtained, solution 2 was replaced by solution 3 (HNO_3 solution). In this way, the heat of dilution of violuric acid into the medium was automatically corrected for. Thus, the baseline shift obtained had to be corrected for the heat of dilution of the HNO_3, which was determined in a separate experiment.

In order to check the accuracy of the microcalorimeter, KOH solutions were neutralized with standard HNO_3. The value obtained ($\Delta H_n = -56.2 \pm 0.2$ kJ mol^{-1}, at 25°C and 0.1 M KNO_3), is in good accordance with a previously reported value [15].

RESULTS AND DISCUSSION

Acidity constants

Aqueous solutions containing dimethylvioluric acid, HMe_2V, ($\sim 5 \times 10^{-3}$ M) and nitric acid ($\sim 10^{-3}$ M), were titrated with a standardized KOH solution (~ 0.1 M). The protonation curve, j vs. pH, was obtained from the potentiometric data (see Fig. 2). The proton association constant, β_{j1}, is given by the slope of the straight line which is obtained on plotting $j/(1-j)$ vs. $[H^+]$. It was also computed using the program Miniquad [16]. The value determined was $\beta_{j1} = (4.075 \pm 0.006) \times 10^4$ (0.1 M KNO_3, 25.0 ± 0.1°C).
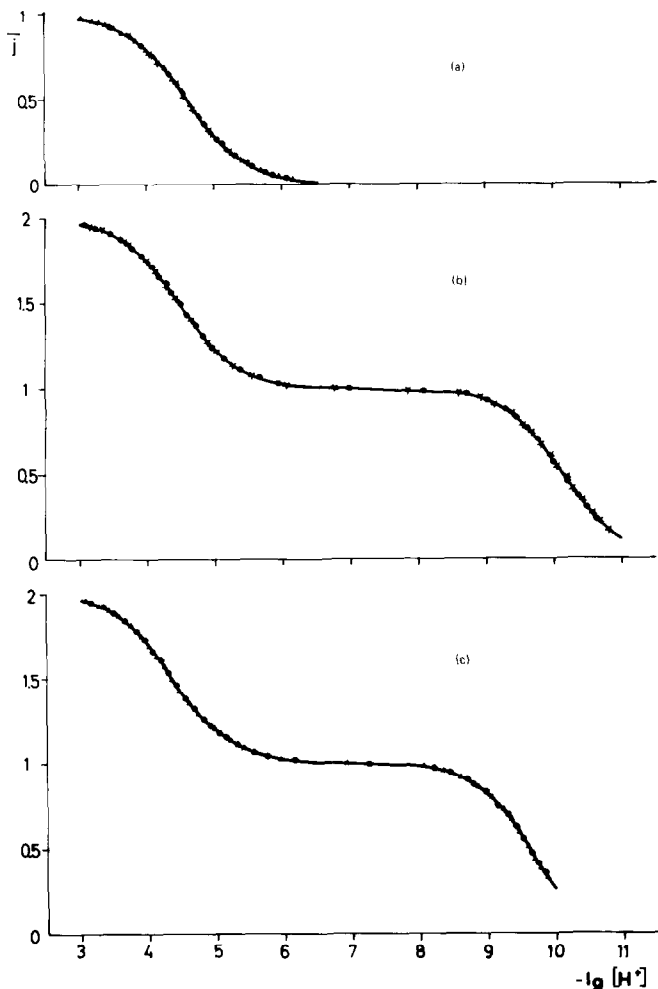
Fig. 2. Protonation curves of violurate anions: (a) Me_2V^-, (b) MeV^{2-}, (c) HV^{2-}. The symbols represent the experimental points. Only a fraction of them is plotted. The solid lines are the theoretical curves calculated with the computed constants.

In a similar way, we have determined the protonation curves of methylvioluric, H_2MeV, and violuric, H_3V, acids (see Fig. 2). From these data we calculated the following proton association constants: methylviolurate, $\beta_{j1} = (1.33 \pm 0.03) \times 10^{10}$, $\beta_{j2} = (4.00 \pm 0.01) \times 10^{14}$; hydrogenviolurate, $\beta_{j1} = (4.36 \pm 0.02) \times 10^9$, $\beta_{j2} = (9.72 \pm 0.06) \times 10^{13}$ (0.1 M KNO_3, $25.0 \pm 0.1°C$).

In the calculus we used more than 100 experimental points from three different experiments, for each acid. A very good fit was obtained comparing the theoretical protonation curves, calculated from the computed constants, with the experimental data (see Fig. 2).

Although violuric acid, H_3V, is a triprotic acid, we have not tried to determine the third acidity constant, because the reaction $HV^{2-} \rightarrow V^{3-} + H^+$

TABLE 1

Acidity constants (pK_a values) of violuric acids

Compound	pK_{a1}	pK_{a2}	$I; t(°C)$	Reference
H_3V	4.35	9.64	0.1 M KNO_3;25°C	This work
	4.52	10.56	18°C	9
	4.34	9.64	0.1 M Na_2SO_4;25°C	18
H_2MeV	4.48	10.12	0.1 M KNO_3;25°C	This work
	4.38	10.08	0.5 M $NaNO_3$;25°C	19
HMe_2V	4.61	–	0.1 M KNO_3;25°C	This work
	4.68	–	0.1 M $NaNO_3$;25°C	20

only occurs at high pH values (pH > 11). In this basic medium the electrode response was not completely satisfactory and violuric acid can undergo some decomposition [17].

The pK_a values of the three violuric acids are shown in Table 1. These values agree well with those previously reported [9,18–20], taking into account the difference in the nature and concentration of the background electrolyte.

The three acids are weak in aqueous solution and their acidity decreases in the series H_3V > H_2MeV > HMe_2V. This is the expected trend considering the inductive effect of the methyl groups, but, as discussed below, it is not an enthalpy but an entropy driven variation.

Ionization enthalpies

For the measurements of ionization enthalpies we adapted Wadso's method [21] to flow microcalorimetry. A solution of potassium hydrogenmethyl-violurate, $HMeV^-$ (~ 0.01 M), and a standardized solution of nitric acid ($\sim 2.5 \times 10^{-3}$ M) were pumped into the mixing cell of the calorimeter. The calorific flows, Φ, corresponding to different degrees of protonation of the anion $HMeV^-$, were recorded varying only the molar flow, V_H, of the nitric acid solution. $HMeV^-$ was in excess with respect to nitric acid in all cases. Some HNO_3 was not consumed in the protonation process because of the observed pH lowering. The amount of HNO_3 used to protonate the $HMeV^-$ anion, V_H^{corr}, was calculated from the measured change in the pH value.

A straight line which intercepts the origin was obtained when plotting $-\Phi^{corr}$ vs. V_H^{corr} (see Fig. 3), Φ^{corr} being the calorific flow corrected for the dilution effect of the HNO_3 acid. Its slope gave the first ionization enthalpy of methylvioluric acid, corresponding to the deprotonation of the oxime group. We have obtained $\Delta H_{i1} = 16.6 \pm 0.2$ kJ mol^{-1}.

Analogously, we have determined the first ionization enthalpy for dimethylvioluric and violuric acids. The values obtained were 15.2 ± 0.2 and 17.1 ± 0.2 kJ mol^{-1}, respectively (0.1 M KNO_3, 25°C).
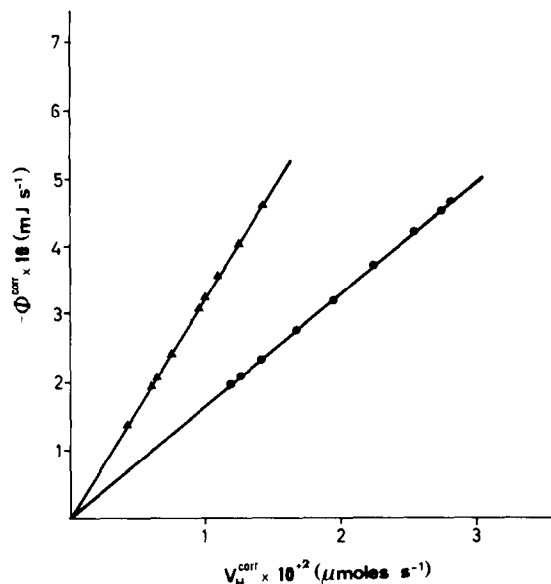
Fig. 3. Plot of calorific flow, $-\Phi^{corr}$, versus molar flow, V_H^{corr}, for the two deprotonation reactions of methylvioluric acid. The ionization enthalpies are given by the slopes of the straight lines (see text).

A solution of methylvioluric acid, H_2MeV ($\sim 5 \times 10^{-3}$ M), partially neutralized with potassium hydroxide to pH $\sim pK_{a2}$, and a solution of nitric acid ($\sim 10^{-3}$ M) were injected into the mixing cell of the calorimeter in order to determine the deprotonation enthalpy of the imino group, i.e., the second ionization enthalpy. The calorific flows, Φ, corresponding to different protonation degrees of the MeV^{2-} anion, were recorded varying the molar flow of the nitric acid solution. V_H^{corr} was calculated as indicated above. Because of the high value of the pH before the reaction (pH ~ 10), the amount of neutralized OH^- was not negligible. Consequently, the calorific flows were corrected not only for the dilution effect of the HNO_3 but also for the water formation effect: $\Phi^{corr} = \Phi - \Phi_{dil} - \Phi_{H_2O}$. The heat of neutralization of OH^- was -56.2 kJ mol^{-1} under our working conditions (see Experimental section). A straight line, whose slope gave the second deprotonation enthalpy of methylvioluric acid, was obtained when plotting $-\Phi^{corr}$ vs. V_H^{corr}. The value obtained is $\Delta H_{i2} = 32.7 \pm 0.5$ kJ mol^{-1}. In the same way, we have determined the value of $\Delta H_{i2} = 33.3 \pm 0.5$ kJ mol^{-1} (0.1 M KNO_3, 25°C) for the second deprotonation enthalpy of the violuric acid. The errors indicated for all of these enthalpy values were estimated for a 95% confidence level and 12–15 degrees of freedom.

Thermodynamic functions $\Delta G^{0\prime}$, $\Delta H^{0\prime}$ and $\Delta S^{0\prime}$ for the deprotonation reactions of the three acids studied are given in Table 2. They are weak acids. Both the enthalpy and entropy variations contribute to this behaviour. All the deprotonation reactions studied are characterized by $\Delta H^0 > 0$ and

TABLE 2

Thermodynamic functions of the deprotonation reactions of violuric acids ($25.0 \pm 0.1°C$, 0.1 M KNO_3) (ΔG and ΔH in kJ mol^{-1}; ΔS in J deg^{-1} mol^{-1})

Compound	First ionization			Second ionization		
	ΔG	ΔH	$-\Delta S$	ΔG	ΔH	$-\Delta S$
H_3V	24.8	17.1	25.8	55.0	33.3	72.8
H_2MeV	25.5	16.6	29.9	57.7	32.7	83.9
HMe_2V	26.3	15.2	37.2			

$\Delta S^0 < 0$. The values of these magnitudes are higher for the imine deprotonation than for that of oxime, having smaller differences between the three compounds for a given ionization step.

The enthalpy variations decrease in the order: $H_3V > H_2MeV > HMe_2V$. This sequence is opposite to that expected taking into account the inductive effect of methyl groups. A simple enthalpy cycle shows that the determining factor is not the dissociation of the O–H bond but the hydration enthalpy of the protonated species.

The entropy variations (negative) increase in the order: $H_3V < H_2MeV < HMe_2V$. Assuming that the ordering effect of the solvent decreases with the substitution of methyl groups for H, a simple entropy cycle shows that the term responsible for the trend is the hydration entropy of the protonated species.

The sequences in the ΔH^0 and ΔS^0 values are opposite, tending to minimize the differences in the acid behaviour of the three violuric acids. Entropy is the dominant term driving the ΔG^0 trend and, hence, the K_a variation. Thus, we show that the "inductive effect" of the methyl groups is not enthalpic but entropic in origin.

Our ionization enthalpies clearly desagree with the reported values for violuric acid [9]. Such a high discrepancy cannot be attributed to the different ionic strength used and we think it is probably due to the experimental method used. The published values of ΔH_i have been determined by Van 'tHoff's method, measuring log K_a at three different temperatures over a range of 24°C. The accuracy of the log K_a values is, according to ref. 9, ± 0.05 log units. This value is about the same order as the measured variations of log K_a with temperature. Thus, the error in ΔH^0 values is larger than 4 kJ mol^{-1} at least. In supporting these considerations our values of ΔH_i, determined by direct calorimetry, differ by ~ 4 kJ mol^{-1} from those obtained using the temperature-dependence method.

REFERENCES

1 A. Weiss and S. Fallab, Helv. Chim. Acta, 37 (1954) 1253.
2 J. Beltrán and J. Faus, J. Chromatogr., 103 (1975) 392.
3 L.V. Ershova and V.V Noskov, Zh. Anal. Khim., 26 (1971) 2406.
4 P.A. Leermakers and W.A. Hoffman, J. Am. Chem. Soc., 80 (1958) 5663.
5 E. Garcia-España, J.M. Moratal and J. Faus, J. Coord. Chem., 12 (1982) 41, and references therein.
6 C. Bremard, B. Mouchel and S. Sueur, Inorg. Chem., 22 (1983) 3562, and references therein.
7 F. Abraham, C. Bremard, B. Mouchel, G. Nowogrocki and S. Sueur, Inorg. Chem., 21 (1982) 3225.
8 J.M. Moratal, M. Julve and J. Faus, Rev. Chim. Miner., 19 (1982) 80, and references therein. .
9 B.R. Singh and R. Ghosh, J. Inorg. Nucl. Chem., 43 (1981) 727.
10 J.D. López, J.M. Salas, M. Melgarejo and C. Valenzuela, An. Quim., 77B (1981) 40.
11 H. Biltz, Chem. Ber., 45 (1912) 3674.
12 H. Biltz and T. Hamburger, Chem. Ber., 49 (1916) 644.
13 G. Arena, R. Cali, V. Cucinotta, S. Musumeci, R. Rizzarelli and S. Sammartano, J. Chem. Soc., Dalton Trans., (1983) 1271.
14 H.S. Rossotti, Talanta, 21 (1974) 809.
15 R.F. Jameson and M.F. Wilson, J. Chem. Soc., Dalton Trans., (1972) 2610.
16 A. Sabatini, A. Vacca and P. Gans, Talanta, 21 (1974) 53.
17 N. Delannoy, A. Delannoy, J. Hennion and J. Nicole, C.R. Acad. Sci. Paris, 287 (1978) 527.
18 C. Bremard, Bull. Soc. Chim. Fr., 5–6 (1975) 953.
19 Y. Vandewalle and J. Nicole, Bull. Soc. Chim. Fr., 9–10 (1978) 363.
20 Y. Vandewalle and J. Nicole, Bull. Soc. Chim. Fr., 7–8 (1977) 593.
21 G. Ojelund and I. Wadso, Acta Chem. Scand., 21 (1967) 1408.