Thermochimica Acta, 12 (1975) 19–23
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

THERMODYNAMICS OF CYCLOALKANE-1,1-DICARBOXYLIC ACIDS IN AQUEOUS SOLUTION

R. CALÍ, S. GURRIERI, E. RIZZARELLI AND S. SAMMARTANO
Istituto di Chimica Generale, Viale A. Doria, 8, 95125-Catania (Italy)
(Received 9 December 1974)

ABSTRACT

The proton ionization in (Na, H)ClO_4 0.1 M aqueous solution of cycloalkane-1,1-dicarboxylic acids at 25°C was studied by means of potentiometric and calorimetric measurements. The thermodynamic functions pK, ΔG, ΔH and ΔS were obtained. The ΔS values were discussed in terms of solute–solvent interaction changes related to the conformational features of the acids.

INTRODUCTION

The ability of Cu^{II} (2,2′-dipyridyl)$^{2+}$ to coordinate, in aqueous solution, cycloalkane-1,1-dicarboxylic acids was recently investigated by means of potentiometric measurements[1,2].

In order to continue the thermodynamic study of these complexes we report the results of potentiometric and calorimetric investigations on the proton ionization of the cycloalkane-1,1-dicarboxylic acids previously employed as ligands: cyclopropane (CPRD), cyclobutane (CBUD), cyclopentane (CPED) and cyclohexane (CHED). The results are discussed on the basis of the entropy change values and are related both with the molecular conformational features of the acids and with the solute–solvent interaction changes during the ionization.

EXPERIMENTAL

Materials

Reagent grade reactants and solvents (Fluka or C. Erba) were employed; when necessary they were purified by conventional methods. CPRD, CBUD and CPED were obtained by basic hydrolysis of the respective diethyl esters[3]. CHED was prepared by treating 1,5-dibromopentane with malonic acid diethyl ester[3]. All the products were crystallized several times from diethyl ether; their purity, checked by potentiometric titrations, was always better than 99.5% and the melting points were: 135°C (CPRD), 162°C (CBUD), 196°C (CPED) and 183°C (CHED).

Potentiometric measurements

Potentiometric measurements for determining the proton ionization constants of the alicyclic acids were carried out under nitrogen constant flow in a thermostated 100-ml glass cell equipped with a magnetic stirrer. A Radiometer potentiometric assembly, composed of a potentiometer Model PHM 52, a glass electrode Model G 2025 C and a calomel electrode Model K 4025, was employed. The temperature was regulated at 25±0.1 °C by means of a Colora NB/DS-997 thermostat. The electrodic system was calibrated by titrating $HClO_4$ with carbonate-free NaOH. The 1–$5 \cdot 10^{-3}$ M alicyclic acid solutions were titrated with a carbonate-free NaOH solution. For each alicyclic acid at least five independent titrations were carried out. CPRD has a low pK_1 value, in order to increase the concentration of H_2A species before each titration, $HClO_4$ was added to the CPRD solutions, so that their molarities were 0.2–$2.5 \cdot 10^{-2}$ M in $HClO_4$. All the titrations were carried out in (Na, H) ClO_4 0.1 M aqueous solutions.

Calorimetric measurements

The calorimetric measurements were performed at 25±0.001 °C employing a LKB precision calorimeter Model 8700, and a 100-ml LKB titration vessel Model 8726-1, equipped with a 50-Ω standard resistance and a 2000-Ω thermistor. The change of thermistor resistance during the titration was recorded by means of a Leeds & Northrup recorder Model Speedomax W. Several series of electrical calibrations were carried out to test the reproducibility of the calorimetric system; the standard deviation of the ε_v mean value was always better than 0.1%. In order to check the accuracy of the calorimeter, a THAM buffer solution was titrated with HCl standard solution; the found enthalpy change value of 11.33 ± 0.05 kcal mol^{-1} was in good agreement with the value obtained by Grenthe et al.[4] under the same experimental conditions.

In order to estimate the proton ionization heats, the alicyclic acid solutions ($\sim 10^{-2}$ M), neutralized until 95% with NaOH standard solution and thermostated until stabilization of the calorimetric system, were titrated stepwise with a $HClO_4$ solution ($\sim 10^{-1}$ M) having the same temperature as the titration vessel. The titrant was delivered from a Radiometer motor burette Model ABU 12b, at 1.25 ml min^{-1} with a 2.5-μl accuracy. The heat equivalent, ε_v, was determined by electrical calibration after each titrant addition. Three solutions of each alicyclic acid were prepared and for each of them at least three titrations were carried out.

Calculations

The dissociation constants were calculated by means of the PMGZ computer program[5] which minimizes the error squares sum: $U(K_1, \beta_2) = \sum_i (\bar{n}_{H,i,obs.} - \bar{n}_{H,i,calc.})^2$, where $\bar{n}_{H,i}$ is the average number of protons bound per ligand. The reaction heat calculations were performed by Dickinson's method[6]; the calorimetric curves were extrapolated to the time for half the temperature rise in all cases, being the heat evolution linear with time both in the calibrations and in the titrations. The reaction heats, corrected for the dilution heat of $HClO_4$ in $NaClO_4$ 0.1 M ($Q_{i,\mathrm{corr.}}$), were calculated considering the calorie unit equivalent to 4.1840 abs. Joules. For each titrant addition the following equilibria were considered:

$$H_2A_{(aq)} \rightleftharpoons H^+_{(aq)} + HA^-_{(aq)} \qquad (K_1, \Delta H_1) \qquad (1)$$

$$HA^-_{(aq)} \rightleftharpoons H^+_{(aq)} + A^{2-}_{(aq)} \qquad (K_{12}, \Delta H_{12}) \qquad (2)$$

$$H_2A_{(aq)} \rightleftharpoons 2H^+_{(aq)} + A^{2-}_{(aq)} \qquad (\beta_2, \Delta H_2) \qquad (3)$$

The enthalpy change values were calculated by means of the PMGQ computer program[7] which minimizes the error squares sum: $U(\Delta H_1, \Delta H_2) = \Sigma\,(Q_{i,\mathrm{corr.}} - Q_{i,\mathrm{calc.}})^2$, where: $-Q_i = \Delta n_{HA^-}\Delta H_1 + \Delta n_{H_2A}\Delta H_2$, being Δn_{HA^-} and Δn_{H_2A} the HA^- and H_2A mmoles increment during the ith titrant addition. The entropy change values were calculated from the relationship: $\Delta G_j = \Delta H_j - T\Delta S_j$. The PMGZ and PMGQ computer programs are based on a direct search of minimum. The $\bar{n}_H$ and Q standard deviation values were better than 0.003 and 0.008, respectively. The uncertainties in the thermodynamic function values were also calculated in terms of standard deviation.

RESULTS AND DISCUSSION

The pK, ΔG, ΔH and ΔS values found for the dissociation reactions (1) and (2) of cycloalkane-1,1-dicarboxylic acids are reported in Table 1.

The low CPRD ΔS_1 value accords with the presence in the CPRD acid molecule both of "conjugation"[8,9] and of intramolecular hydrogen bonding. The latter might be supposed to be due to: (a) the difference between pK_{12} and pK_1 values[10], (b) X-rays data[11], (c) the closeness of the ΔS_1 value to that of maleic acid (-8.5 e.u.mol^{-1}) (ref. 12), for which there are spectroscopic evidences of intramolecular hydrogen bonding[13].

The ΔS_1 values of CBUD and CPED are close to each other (as in the case of the corresponding monocarboxylic acids)[14] and to the value ($\Delta S_1 = -12.0$ e.u.mol^{-1}) reported for the malonic acid[12].

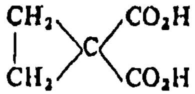
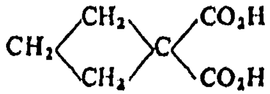
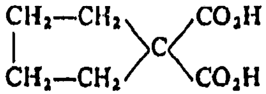
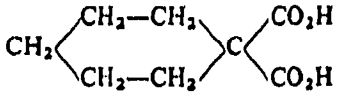
The CBUD and CPED acids have different steric features of the skeleton because the CBUD acid ring is substantially planar[15] whereas that of the CPED acid is half chair[16]; moreover, by increasing cycloalkane ring terms, the bond angle between the carboxylic groups decreases.

Presumably the typical conformation features of the five-membered ring reduce the interaction between the carboxylic groups as a consequence of "non-bonded interactions"[17]. These, however are not present in the CBUD acid because its ring is planar, and therefore permit the CPED and CBUD acids to behave similarly in their ability to change the orientation of the solvent molecules during the first ionization step.

The ΔS_1 value of the CHED acid, which is higher than those of CBUD and

TABLE 1

THERMODYNAMIC FUNCTIONS FOR THE IONIZATION OF CYCLOALKANE-1,1-DICARBOXYLIC ACIDS IN (Na, H) ClO_4 0.1 M AQUEOUS SOLUTION

Acid	*Formula*	*Step*	p*K*[a]	Δ*G* (*kcal mol*$^{-1}$)	Δ*H* (*kcal mol*$^{-1}$)	Δ*S* (*e.u. mol*$^{-1}$)
CPRD		1	1.632±0.025	2.225±0.034	−0.310±0.017	−8.50±0.13
		12	7.197±0.009	9.813±0.012	+0.385±0.007	−31.62±0.05
CBUD		1	2.922±0.002	3.984±0.003	−0.259±0.016	−14.23±0.05
		12	5.454±0.002	7.436±0.003	−0.805±0.009	−27.64±0.03
CPED		1	3.081±0.002	4.201±0.003	−0.063±0.016	−14.30±0.05
		12	5.769±0.002	7.866±0.003	−0.902±0.010	−29.41±0.04
CHED		1	3.270±0.002	4.459±0.003	−1.045±0.022	−18.46±0.07
		12	5.683±0.001	7.749±0.001	+0.079±0.011	−25.72±0.04

---

[a] These values agree with those of refs. 19 and 20.

CPED, may be accounted for by the increasing orientation abilities on the solvent molecules, owing to the "stiffening" effect[14,18] and to non-bonded interactions due to the chair conformation of the cyclohexane ring. This behaviour accords with the ΔS_1 value of succinic acid (-16.6 e.u.mol^{-1}) (ref. 12) where the two carboxylic groups are separated by two carbon atoms.

The ΔS_{12} values, reported for the second ionization step, agree with the trends evidenced for the ΔS_1 values.

ACKNOWLEDGMENT

We are grateful to the Consiglio Nazionale delle Ricerche, Roma, for support of this research.

REFERENCES

1 R. P. Bonomo, S. Musumeci, E. Rizzarelli and S. Sammartano, *Atti VI Conv. Naz. Chim. Inorg., Firenze*, (1973) 463.
2 R. Maggiore, S. Musumeci, E. Rizzarelli and S. Sammartano, *Boll. Accad. Gioenia*, XII (1974) 569.
3 A. I. Vogel, *J. Chem. Soc.*, (1929) 1487.
4 I. Grenthe, H. Ots and O. Ginstrup, *Acta Chem. Scand.*, 24 (1970) 1067.
5 S. Musumeci, E. Rizzarelli, S. Sammartano and R. P. Bonomo, in preparation.
6 I. Wadsö, *Sci. Tools*, 13 (1963) 33.
7 S. Musumeci, C. Rigano and S. Sammartano, *Boll. Accad. Gioenia*, XII (1974) 599.
8 A. R. Mochel, J. E. Boggs and P. N. Skancke, *J. Mol. Struct.*, 15 (1973) 93.
9 G. Daviaud and Ph. Miginiac, *Tetrahedron Lett.*, 11 (1972) 997.
10 L. Eberson and I. Wadsö, *Acta Chem. Scand.*, 17 (1963) 1552.
11 A. M. M. Meester, H. Schenk and H. C. Mac Gillary, *Acta Crystallogr., Sect. B*, 27 (1971) 630.
12 J. J. Christensen, R. M. Izatt and L. D. Hansen, *J. Amer. Chem. Soc.*, 89 (1967) 213.
13 E. J. King, *Acid-Base Equilibria*, Macmillan, New York, N.Y., 1965.
14 J. J. Christensen, D. E. Smith, M. D. Slade and R. M. Izatt, *Thermochim. Acta*, 4 (1972) 17.
15 L. Soltzberg and T. N. Margulis, *J. Chem. Phys.*, 55 (1971) 4907.
16 R. L. Lipnick, *J. Mol. Struct.*, 21 (1974) 423.
17 L. S. Bartell, *J. Chem. Educ.*, 45 (1968) 754.
18 J. W. Larson and L. G. Hepler, in J. F. Coetzee and C. D. Ritchie (Eds.), *Solute–Solvent Interactions*, Marcel Dekker, New York, N.Y., 1969, p. 23.
19 G. Ostacoli, E. Campi, A. Vanni and E. Roletto, *Ric. Sci.*, 36 (1966) 427.
20 E. Roletto, A. Vanni and G. Ostacoli, *J. Inorg. Nucl. Chem.*, 34 (1972) 2817.