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THERMODYNAMICS OF PROTON IONIZATION IN DILUTE AQUEOUS SOLUTION

XVI*. ΔG° (pK), ΔH°, ΔS°, AND ΔC_p° VALUES FOR PROTON IONIZATION FROM SEVERAL CYCLOALKANECARBOXYLIC ACIDS AT 10, 25, AND 40°

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SUMMARY

A calorimetric study has been made of proton ionization in dilute aqueous solution from cycloalkanecarboxylic acids at 10, 25, and 40°. Values of ΔS° are calculated by combining the resulting ΔH° values with ΔG° values obtained from the literature or determined by calorimetric measurements. Values of ΔC_p° were calculated from the variation of the ΔH° values with temperature. The trends in ΔS° and ΔC_p° are compared to the corresponding values for straight chain aliphatic carboxylic acids.

INTRODUCTION

This study was undertaken as part[1] of a program to determine the thermodynamic quantities associated with proton ionization from a variety of donor-atom types in aqueous solution. Previously, the effects of substituents on the thermodynamic quantities for proton ionization from straight chain aliphatic acids have been reported[2,3]. The present study deals with proton ionization from cycloalkanecarboxylic acids and includes a comparison between the thermodynamic quantities for proton ionization from cycloalkane and straight chain carboxylic acids.

EXPERIMENTAL

Materials. — The following compounds were obtained in the best grade available from the indicated sources: Baker grade cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, and cyclohexanecarboxylic acid (Baker); practical cyclopropanecarboxylic acid (Eastman); cyclohexylacetic acid (Aldrich Chemical).

All acids were fractionally distilled under reduced pressure. Portions of each acid were then treated with slightly less than a stoichiometric amount of sodium

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hydroxide (Baker, Analyzed Reagent, carbonate free, 50% solution). The resultant solutions of the salts were washed with benzene and ether, the water was slowly evaporated, and ethanol was added until the solutions became slightly turbid. Following precipitation and separation from the cooled solutions, the salts were recrystallized twice from an alcohol–water solution and dried under vacuum.

Procedures. — The titration calorimeter used in this study has been described[4,5]. This calorimeter makes possible the measurement of heats of 1–10 cal with a precision of 0.1%. Data for ΔH determinations were obtained by titrating solutions of the sodium salts of the cyclocarboxylic acids with standard perchloric acid (Baker and Adamson) solutions at 10, 25, and 40°. At least five calorimetric titrations were made for each acid at each temperature with the ionic strength, μ, in each case being <0.02.

The pK values were either taken from the literature (see Table I) or determined using a calorimetric titration procedure[5–8] in which solutions of the cycloalkanecarboxylic acids were titrated with standard 3-picoline (Baker) solutions.

Calculations. — The general method used to calculate ΔH values from the calorimetric titration data has been described[5,6,9]. Values for the heats of dilution of perchloric acid and 3-picoline were determined calorimetrically at 10, 25, and 40°. Values for the heat of ionization of water at 10 and 40° were determined by us[10] to be 14.216 and 12.695 kcal/mole, respectively, and that at 25° (13.335 kcal/mole) was taken from the literature[11]. At the low ionic strength ($\mu<0.02$) used in the calorimetric determinations, ΔH values do not vary significantly[12] with μ; therefore, they were assumed to be equal to ΔH° values. The standard state to which ΔH° refers is defined to be an ideal 1 M solution behaving as an infinitely dilute solution. The calculations were aided by a P. E. Liberscope L-3055 computer. The computer programs (Fortran IV), input data, and output data for each run are available[13].

RESULTS

In Table I are presented the pK, ΔG°, ΔH°, ΔS°, and ΔC_p° values determined in this study. All the data in Table I refer to $\mu = 0$. The accuracy of the ΔH° values is estimated to be ± 50 cal. This estimate was obtained from a consideration of the accuracy of the values previously obtained for the heat of ionization of water using the same equipment. The reported precision limits for the ΔH° values in Table I are given as the standard deviation of these values for each set of runs for a given acid. The combined uncertainties in the pK and ΔH° values will result in an estimated precision of ± 0.2 cal/mole/degree in the ΔS° values. The combined uncertainties in the ΔH° values at each temperature result in an estimated precision of ± 5 cal/mole/degree in the ΔC_p° values.

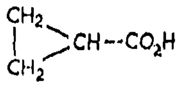
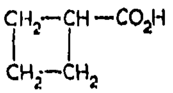
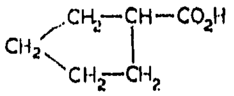
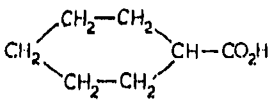
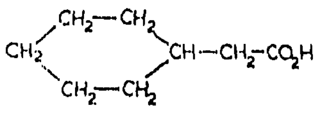
DISCUSSION

Presented in Table II is a comparison of like data for proton ionization from cycloalkanecarboxylic acids and from related straight chain, methyl and ethyl

TABLE I

THERMODYNAMIC QUANTITIES[a] FOR THE REACTION $HA = H^+ + A^-$

Values are valid for aqueous solution at $\mu = 0$

HA	*Formula*	*Temp. (°C)*	*pK*	*ΔG°* (*kcal/mole*)	*ΔH°* (*kcal/mole*)	*ΔS°* (*cal/mole/degree*)	*ΔC°$_p$* (*cal/mole/degree*)
Cyclopropane carboxylic acid		10	4.93	6.38	0.52±0.01	−20.7	−40
		25	4.827^b	6.585	−0.01±0.01	−22.1	
		40	4.92	7.04	−0.67±0.01	−24.6	
Cyclobutane carboxylic acid		10	4.60	5.96	−0.08±0.01	−21.3	−43
		25	4.785^b	6.527	−0.68±0.02	−24.2	
		40	4.82	6.90	−1.38±0.01	−26.4	
Cyclopentane carboxylic acid		10	4.67	6.05	0.04±0.01	−21.2	−42
		25	4.905^b	6.692	−0.52±0.03	−24.2	
		40	4.96	7.10	−1.23±0.05	−26.6	
Cyclohexane carboxylic acid		10	4.62	5.98	0.23±0.02	−20.3	−37
		25	4.899^c	6.683	−0.37±0.02	−23.7	
					−0.92^d		
		40	5.01	7.17	−0.91±0.05	−25.8	
Cyclohexyl acetic acid		10	4.45	5.77	−0.56±0.01	−22.4	−49
		25	4.51	6.15	−1.39±-0.01	−25.3	
		40	4.55	6.52	−2.04±0.01	−27.3	

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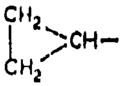
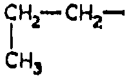
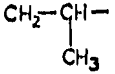
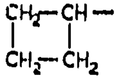
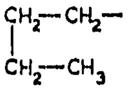
[a] The precision of the p*K* values is ±0.01 p*K* unit while that of the *ΔH°* values is indicated in each case. The precision values are calculated as standard deviations. [b] Ref. 20. [c] Ref. 21. [d] Ref. 12.

TABLE II

COMPARISON OF THERMODYNAMIC QUANTITIES OF CYCLOALKANECARBOXYLIC ACIDS WITH STRAIGHT CHAIN, METHYL AND ETHYL SUBSTITUTED ALIPHATIC ACIDS

All values valid at $\mu = 0$ and 25 °C

Acid	*Formula*[a]	ΔG° (*kcal/mole*)	ΔH° (*kcal/mole*)	ΔS° (*cal/mole/degree*)	ΔC_p° (*cal/mole/degree*)
Cyclopropane carboxylic acid		6.59	−0.01	−22.1	−40
Butanoic acid	 $CH_3-CH_2-CH_2-$	6.58[b]	−0.64[c]	−24.2	−35
2-Methylpropanoic acid	 $CH_3-CH(CH_3)-$	6.62	−0.75[d]	−24.7	−36
Cyclobutane carboxylic acid		6.53	−0.68	−24.2	−43
Pentanoic acid	 $CH_3-CH_2-CH_2-CH_2-$	6.61	−0.66[d]	−24.4	−32

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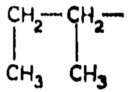
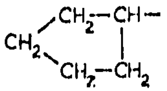
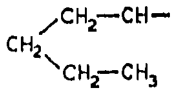
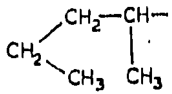
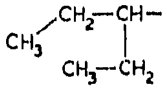
[a] The formula given corresponds to R in R–COOH. [b] Ref. 22. [c] Ref. 3. [d] Ref. 2.

TABLE II (*continued*)

Acid	*Formula*[a]	*$\Delta G°$* (*kcal/mole*)	*$\Delta H°$* (*kcal/mole*)	*$\Delta S°$* (*cal/mole/degree*)	*$\Delta C_p°$* (*cal/mole/degree*)
2-Methylbutanoic acid		6.67	−1.24[d]	−26.1	
Cyclopentane carboxylic acid		6.69	−0.52	−24.2	−42
Hexanoic acid		6.66	−0.64[d]	−24.5	−33
2-Methylpentanoic acid		6.54	−1.28[d]	−26.2	−27
2-Ethylbutanoic acid		6.48	−1.97[d]	−28.4	−25

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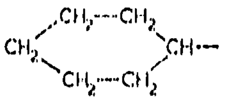
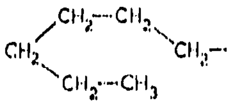
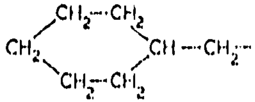
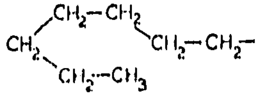
[a]The formula given corresponds to R in R-COOH. [b]Ref. 22. [c]Ref. 3. [d]Ref. 2.

TABLE II (*continued*)

Acid	*Formula*[a]	ΔG° (*kcal/mole*)	ΔH° (*kcal/mole*)	ΔS° (*cal/mole/degree*)	ΔC_p° (*cal/mole/degree*)
Cyclohexane carboxylic acid		6.68	−0.37	−23.7	−37
Heptanoic acid		6.67	−0.61[d]	−24.4	−33
Cyclohexylacetic acid		6.15	−1.39	−25.3	−49
Octanoic acid		6.68	−0.62[d]	−24.5	

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[a] The formula given corresponds to R in R–COOH. [b] Ref. 22. [c] Ref. 3. [d] Ref. 2.

substituted aliphatic acids. Ionization of protons from straight chain carboxylic acids results in the chain being repelled from the negatively charged carboxylic group[14]. In the corresponding cycloalkanecarboxylic acids, the chain is fixed in place. This difference between straight chain and cycloalkanecarboxylic acids should be reflected in their respective ΔH°, ΔS°, and ΔC_p° values. The ΔG° values for the cycloalkanecarboxylic acids and the related straight chain or substituted acids are nearly the same. This results in the ΔH° values compensating for the less negative ΔS° values of the cycloalkanecarboxylic acids[15,16].

Statistical explanations have been used to describe the ΔS° effect in straight chain acids[15]. The charged anion imposes order on the surrounding solvent molecules which interferes with internal rotation[17,18]. This effect is also interpreted as a "stiffening" of the chain, which occurs because the region of low dielectric constant is repelled from an electrostatic charge[15,16,19]. This is observed in the straight chain acids where the ΔS° values become more negative as the chain becomes longer. The cycloalkanecarboxylic acids, in which the chain cannot straighten out, have ΔS° values which are less negative than the corresponding ΔS° values for the straight chain acids, however the differences are small.

The ΔC_p° values for proton ionization from the cycloalkanecarboxylic acids are more negative than the values for the similar straight chain acids. If we consider the reaction

$$\mathrm{HA} + (m+n)\mathrm{H_2O} = \mathrm{H(H_2O)}_m^+ + \mathrm{A(H_2O)}_n^-$$

the ΔC_p° for the reaction equals the sum of the heat capacities of the products minus the sum of the heat capacities of the reactants. The heat capacities of the cyclic and straight chain carboxylic acids (HA) are nearly the same, and the heat capacity of $\mathrm{H(H_2O)}_m^+$ is the same for all acids. The heat capacity of the water which is hydrated to A^- is lower than that of the water in the solvent before ionization occurs. The cycloalkanecarboxylic acids, in general, have fewer waters of hydration than do the straight chain acids .This results, taking into account the heat capacity of the water on both sides of the reaction, in the cycloalkanecarboxylic acids having more negative ΔC_p° values than the corresponding straight chain, methyl and ethyl substituted acids.

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