Effects of Alkyl Chain Length on the Thermodynamics of Proton Ionization from Arsonic and Arsinic Acids

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$\Delta G°$, $\Delta H°$, and $\Delta S°$ values are reported for the two proton ionizations from several n-alkylarsonic acids (methyl, ethyl, propyl, butyl, pentyl, and hexyl) and from several protonated di-n-alkylarsinic acids (methyl, ethyl, propyl, butyl, and pentyl) in aqueous solution at 25°. The $\Delta G°$ values were determined from pH measurements, and the $\Delta H°$ values were determined calorimetrically. The variations in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with alkyl chain length found for both the arsonic and arisinic acid ionizations differ from hydrocarbon chain lengthening effects on the thermodynamics of proton ionization previously reported for protonated amines, protonated amino-acids, and carboxylic acids.

It has been reported previously[1-6] that the thermodynamics of ionization of a head group is affected by the length of an alkyl group attached to the ionizing head group. Proton ionization from protonated amines, protonated amino-acids and carboxylic acids, and the formation of bis(n-alkylamino)silver(I) complex ions have all shown this chain length effect. The variations in $\Delta G°$ with alkyl chain length have been found to be minimal in all these studies with the changes in the corresponding $\Delta H°$ and $T\Delta S°$ values compensating each other to a large extent. The general trend with increasing chain length is that both $\Delta H°$ and $T\Delta S°$ values become more positive for isoelectric reactions (*e.g.* $H^2A^+ \longrightarrow H^+ + HA$) and become more negative for ionogenic reactions (*e.g.* $HA \longrightarrow H^+ + A^-$) while $\Delta G°$ values are largely unaffected in either type of reaction. The explanations proposed to account for the compensation of $\Delta H°$ and $T\Delta S°$ with increasing hydrocarbon chain length are: (a) the hydrocarbon chain stiffening under the influence of a charged head group and (b) the charged head group establishing a structured solvation shell which would restrict rotation of the alkyl group. Both these effects would result in a loss of enthalpy and entropy of rotation in the charged molecule relative to the neutral molecule.

The purpose of the present study was (a) to determine $\Delta G°$, $\Delta H°$, and $\Delta S°$ values for proton ionization from n-alkylarsonic acids (alkyl = CH_3—C_6H_{13}) and di-n-alkylarsinic acids (alkyl = CH_3—C_5H_{11}) and (b) to compare the effects of alkyl chain lengthening in the arsonic and arsinic acids with those observed for the carboxylic acids and protonated amines. This study was of interest because of the different ionizing head group and especially since the second ionization from the arsonic acids involves a charge type (separation of a proton from the field of a double negative charge) not duplicated by the protonated amines, amino-acids, or carboxylic acids. Additional information on the underlying causes of the trends observed with increasing hydrocarbon chain length was also expected from the study of the arsinic acids, as a second n-alkyl group is attached to the ionizing head group in these molecules.

EXPERIMENTAL

Materials.—Methyl-, ethyl-, and butyl-arsonic acids were prepared as described by Quick and Adams.[7] Propylarsonic acid was purchased from Eastman Chemicals and was recrystallized from ethanol. n-Pentyl and n-hexyl-arsonic acids as well as the diethyl-, di-n-butyl-, and di-n-pentylarsinic acids were a generous gift from Dr. K. Irgolic, Texas A and M University. Dimethylarsinic acid was purchased from K and K Laboratories and used without further purification. The purity of all the compounds was verified by m.p.[7-9] and by equivalent weight determinations, and all were found to be >99% pure. Perchloric acid solutions were prepared from Baker Analyzed reagent grade 70% perchloric acid and standardized by volumetric titration against primary standard grade Fisher THAM using a visual endpoint indicator. The sodium hydroxide solutions were standardized by volumetric titration against standardized perchloric acid solutions. All solutions were prepared using freshly boiled, doubly distilled water.

Equipment.—A Beckman research pH meter, model 1019, was used for the pH measurements. The pH meter was equipped with a Beckman E-3 glass electrode (0—14 pH range) and an Orion Ag–AgCl single junction reference electrode, model 90-01. The buffer solutions used for standardization of the pH meter were pH 6.862 phosphate and pH 4.008 potassium hydrogen phthalate, both prepared using National Bureau of Standards (NBS) materials according to NBS instructions.

The calorimetric measurements were made using a Tronac thermometric titration calorimeter, model 1000A, which has previously been described.[10] A typical run consisted of 30 data points taken in the fore period, 62 data points taken in the main period, and 30 data points taken in the after period at intervals of 20 s.[11] The burette delivery rate used

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in this study was 0.1660 ml min^{-1}. All measurements were made at (25.0 ± 0.1)°.

Procedure.—For the $\Delta G°$ determinations, solutions of the arsonic and arsinic acids in the completely protonated form (100 ml, 0.01M) were titrated with a standard sodium hydroxide solution (0.6M). Several titrations were carried out on each of the compounds, and several pH measurements were taken in the buffer regions.

For the ΔH determinations, 99.91 ml of the anion form of the arsonic and arsinic acids were titrated with a standard perchloric acid solution (1.009M).

Calculations.—The procedure for calculation of $\Delta G°$ values from the pH titration data has previously been described.[12] The $\Delta G°$ values were determined at a single low ionic strength and extrapolated to $\mu = 0$ by use of the Debye–Hückel equation (1) where a is the distance parameter and μ is the ionic strength.[13] The value used in this study for a was 5 Å.

$$\log \gamma_i = -(0.5095)(\mu)^{\frac{1}{2}}/[1.0 + (0.3288)(a)(\mu)^{\frac{1}{2}}] \quad (1)$$

The method used to calculate the heat change values, Q_i, from the temperature time data in the main period of the thermogram, has previously been described.[11,14] The Q values at each point were corrected for the heat of formation of water and the heat of dilution of the perchloric acid titrant. The ΔH values were calculated from a least-squares fit of the corrected Q values and the calculated species distribution. Since the ΔH values were determined at a low ionic strength, it was assumed that $\Delta H° = \Delta H^{\mu}$.

The enthalpy of dilution of the perchloric acid titrant was taken from ref. 15, and all computations were done on an IBM 360-67 computer.

RESULTS

The values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ determined in this study for the two proton ionizations from the n-alkylarsonic acids are given in Table 1 and those for the di-n-alkylarsinic acids in Table 2. The error limits are the average deviations from the mean for a series of four determinations.

TABLE 1

Thermodynamics of proton ionization from arsonic acids ($RAsO_3H_2$) at 25°

R	Reaction [a]	$\Delta G°$/ kcal mol^{-1} [b]	$\Delta H°$/ kcal mol^{-1} [b]	$\Delta S°$/cal mol^{-1} K^{-1}
Methyl	(1)	5.71 ± 0.04	−1.65 ± 0.03	−24.7
	(2)	11.96 ± 0.05	+1.40 ± 0.01	−35.4
Ethyl	(1)	5.78 ± 0.05	−1.83 ± 0.01	−25.5
	(2)	12.53 ± 0.05	+1.53 ± 0.03	−36.9
Propyl	(1)	5.92 ± 0.03	−1.53 ± 0.01	−25.0
	(2)	12.76 ± 0.10	+1.93 ± 0.02	−36.3
Butyl	(1)	5.95 ± 0.04	−1.56 ± 0.03	−25.2
	(2)	12.69 ± 0.01	+1.88 ± 0.02	−36.3
Pentyl	(1)	5.91 ± 0.01	−1.53 ± 0.01	−25.0
	(2)	12.80 ± 0.01	+1.87 ± 0.01	−36.7
Hexyl	(1)	5.91 ± 0.01	−1.54 ± 0.04	−25.0
	(2)	12.83 ± 0.01	+1.89 ± 0.04	−36.7

[a] Reaction (1) is $RAsO_3H_2 \longrightarrow RAsO_3H^- + H^+$; reaction (2) is $RAsO_3H^- \longrightarrow RAsO_3^{2-} + H^+$. [b] Deviations are the average from the mean.

DISCUSSION

To a first approximation, $\Delta S°$ depends only on the nature of the ionization process (*i.e.*, $\Delta S°$ is more negative for an ionogenic than for an isoelectric reaction). The values of $\Delta S°$ for proton ionization from the carboxylic acids (−22 to −25 cal mol^{-1} K^{-1}) and the first ionization of arsonic acids are nearly equal, $\Delta S°$ for ionization from protonated dialkylamines (*ca.* −10 cal mol^{-1} K^{-1}) and protonated dialkylarsinic acids are also approximately equal, and the $\Delta S°$ for ionization of branched chain carboxylic acids (*ca.* −28 cal mol^{-1} K^{-1}) is comparable to that for ionization from the neutral arsinic acids.

TABLE 2

Thermodynamics of proton ionization from arsinic acids (R_2AsO_3H) at 25°

R	Reaction [a]	$\Delta G°$/ kcal mol^{-1} [b]	$\Delta H°$/ kcal mol^{-1} [b]	$\Delta S°$/cal mol^{-1} K^{-1}
Methyl	(1)	2.43 ± 0.45	−0.84 ± 0.35	−11.0
	(2)	8.37 ± 0.07	−0.63 ± 0.03	−30.2
Ethyl	(1)	2.09 ± 0.04	−1.83 ± 0.08	−13.2
	(2)	8.76 ± 0.01	−0.88 ± 0.01	−32.3
Propyl	(1)	2.24 ± 0.28	−1.89 ± 0.48	−13.9
	(2)	8.89 ± 0.01	−0.65 ± 0.04	−32.0
Butyl	(1)	2.02 ± 0.08	−1.89 ± 0.03	+13.1
	(2)	8.90 ± 0.01	−0.49 ± 0.05	−31.5
Pentyl	(1)	2.30 ± 0.03	−1.51 ± 0.09	−12.8
	(2)	8.91 ± 0.01	−0.31 ± 0.01	−30.9

[a] Reaction (1) is $R_2AsO_2H_2^+ \longrightarrow R_2AsO_2H + H^+$; reaction (2) is $R_2AsO_2H \longrightarrow R_2AsO_2^- + H^+$. [b] Deviations are average from the mean.

The Figure presents a plot of $\Delta S°$ against the number of methyl groups for proton ionization from various parent methylated derivatives. The $\Delta S°$ values for the amines, thiols, and carboxylic acids were taken from ref. 16, and the symmetry correction for ionization has been applied.[17] This plot not only shows that the addition of an alkyl group makes a negative contribution to the $\Delta S°$ for proton ionization from all these molecules but also that the slope of $\Delta S°$ against number of methylations is approximately constant. The change in $\Delta S°$ is approximately given by equation (2) where $\Delta S_0°$ is the entropy

$$\Delta S° = \Delta S_0° - 6N \text{ cal mol}^{-1} \text{ K}^{-1} \quad (2)$$

change for proton ionization from the parent acid and N the number of alkyl groups attached to the ionizing head group. The arsenic acids and glycolic acid show the effect of substituting an alkyl group for a hydroxy-group while all others show the effects of hydrogen replacement. The amines yield a neutral molecule on proton ionization while all others yield an anion. However, the trend of the change in $\Delta S°$ with alkyl substitution is

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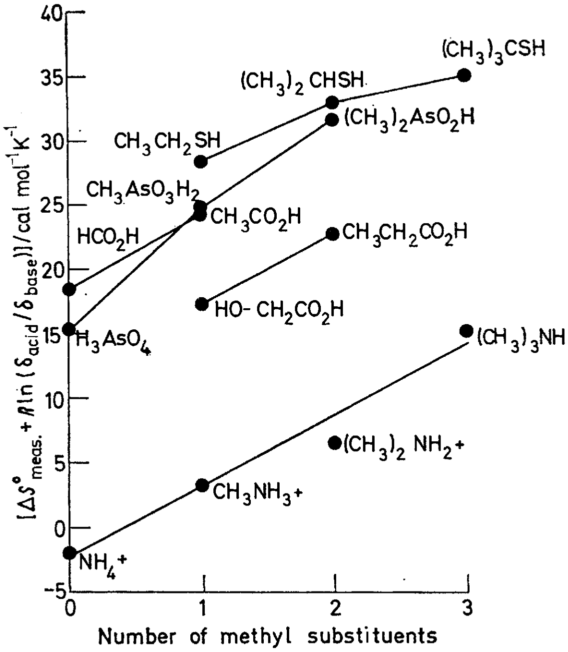
apparently insensitive to these ' details '. It should be emphasized that the loss of alkyl rotation entropy upon ionization from the protonated amines is completely inconsistent with the theories that the charged head group ' freezes ' the alkyl group by (a) repulsion of the low dielectric region from the vicinity of the head group charge and (b) the structured solvation shell of the charged head group restricting rotation of the alkyl group. Both effects would result in the loss of entropy of rotation in the charged molecule relative to the neutral molecule. The ultimate theory will have to explain the loss of rotational entropy of the alkyl substituent (*ca.* 6 cal mol^{-1} K^{-1}) [18] in the deprotonated acid whether it is neutral or anionic and at the same time account for the similarity of replacement of either a hydroxy-group or hydrogen with an alkyl group. No systematic change in $\Delta H°$ for proton ionization is found on substitution of an alkyl group for either a hydrogen or hydroxy-group.



Dependence of the entropy change for proton ionization on the number of methyl (or alkyl) substituents. Plot of $-\Delta S$ against the number of methyl groups attached to the ionizing head group for four different parent acids. The entropy changes have been corrected for symmetry number,[17] *i.e.* $-\Delta S = -[\Delta C°_{measured} + R\ln(\sigma_{acid}/\sigma_{base})]$

Both ionizations from the arsonic acids are ionogenic reactions ($H_2A \longrightarrow H^+ + HA^-$, and $HA^- \longrightarrow H^+ + A^{-2}$). Previous studies [1-6] predict that $\Delta G°$ would vary little with increasing hydrocarbon chain length while $\Delta H°$ and $\Delta S°$ would decrease for both proton ionizations from the n-alkylarsonic acids. The first arsonic acid ionization would be expected to show trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with chain length similar to those previously reported for carboxylic acids.[4] The second ionization involves a charge type not studied previously, however the predicted chain lengthening effects should again show the same trends in $\Delta H°$ and $\Delta S°$ with the changes being larger due to the increased charge on the resultant acid anion. The first ionization from protonated di-n-alkylarsinic acids is an isoelectric reaction ($H_2A^+ \longrightarrow H^+ + HA$) while the second is an ionogenic reaction ($HA \longrightarrow H^+ + A^-$). The first reaction is analogous to ionization from protonated amines while the second is comparable to carboxylic acids. Previous studies [1-6] allow the prediction of trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with changing hydrocarbon length assuming that the second alkyl group does not alter these trends but simply enlarges them due to the loss of enthalpy and entropy of rotation of both alkyl groups in the ionic form relative to the neutral molecule. The first ionization from the arsinic acids would show compensation of $\Delta H°$ and $\Delta S°$ ($\Delta G°$ would vary little with increasing chain length) and both $\Delta H°_1$ and $T\Delta S°_1$ would increase if the pattern of the protonated amines was to be paralleled. The second ionization would again show compensation with $\Delta H°_2$ and $T\Delta S°_2$ decreasing if the pattern of the carboxylic acids was to be repeated. For both reactions the changes in $\Delta H°$ and $\Delta S°$ would be larger due to the presence of the second alkyl group.

The actual trends in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with increasing chain length for both the arsonic and arsinic acids are different from those predicted above. Some changes in the values of the thermodynamic parameters are smaller than expected and the direction of some changes is opposite to that predicted. In some instances compensation of changes in $\Delta H°$ by changes in $\Delta S°$ does not occur. The current explanations [1-6] for compensation of $\Delta H°$ and $T\Delta S°$ and the variations in $\Delta G°$, $\Delta H°$, and $\Delta S°$ with changing hydrocarbon chain length fail in predicting the thermodynamic trends for proton ionization from both the n-alkylarsonic acids and the di-n-alkylarsinic acids. A theory explaining the effects of hydrocarbon chain lengthening on the thermodynamics of proton ionization from protonated amines, carboxylic acids, arsonic acids, arsinic acids, and any ionizable head group with an alkyl substituent eludes us at present. However, two observations from the present study are worth noting. (1) The trends with chain length are different for analogous reactions (*e.g.* first arsonic acid ionization and carboxylic acids, or first arsinic acid ionization and protonated amines) implies that the nature of the head group must be as important as the charge or reaction type in determining the effects of alkyl chain length on the reaction thermodynamics. (2) The distance over which a head group extends its influence must depend upon head group solvation processes and this may account for the change in slope of the thermodynamic trends at different alkyl chain lengths for various ionizing groups.

Conclusions.—That the chain lengthening effects and substituent effects reported on and discussed here are inexplicable at present must be due to the complex nature of the solvent (water) and poorly understood solvation processes. The often noted compensation of ΔH and

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$T\Delta S$ is very probably the result of either the making or breaking of water structure (*e.g.*, when water stucture is disrupted the entropy change is favourable while the enthalpy change is unfavourable due to the loss of hydrogen bonds). More insight into these phenomena might be gained if studies similar to the one reported here were done over a range of temperatures and perhaps in mixed or in other protic solvents.

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