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# Intramolecular Solvation of Carboxylate Anions in the Gas Phase

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Proton exchange reactions between acetate, *n*-butanoate, 2-ethylhexanoate, and *n*-decanoate were studied experimentally by the use of PHPMS and theoretically by the use of ab initio methods. The occurrence of a curvature in some of the van't Hoff plots suggests isomerization of at least one of the participants in the equilibrium. This isomerization is suggested to be an intramolecular solvation of the carboxylate anions via unconventional hydrogen bonding. These interactions are discussed in terms of charge distributions in the unfolded and folded conformers of the carboxylates. Thermochemical values for the intramolecular solvation were deconvoluted from the curved van't Hoff plots by a fitting procedure. The thermochemical data for the intramolecular solvation was used to calculate the conformer composition of the carboxylate anions. Various properties related to the intramolecular solvation of the carboxylate anions are discussed.

## 1. Introduction

Intramolecular solvation of neutrals and ions is a common occurrence in both solution and the gas phase. The simplest form of intramolecular solvation is the formation of an intramolecular hydrogen bond in bifunctional compounds. Intramolecular hydrogen bonding can significantly influence the structure and properties of organic compounds. In particular, intramolecular hydrogen bonds are often responsible for determining the predominant conformers in both solution[1,2] and the gas phase.[3−7] Intramolecular hydrogen bonding is also prevalent for polyfunctional compounds and thus plays an important role in many biological systems. Many organic and enzymatic reactions proceed through protonated intermediates or involve direct hydrogen bonding such as those involving proteins or DNA complexes.

Many workers have studied intramolecular solvation, and the phenomenon has been characterized both theoretically and experimentally in gaseous ionic species such as diols,[3,4] diamines,[5−7] polyamines,[8] diethers,[7,9] diketones,[7,10] amides and amino acid derivatives,[11] amino alcohols,[6] diaminonaphthalenes,[12] carboxylic acid derivatives,[13] and methoxyalcohols.[14] Intramolecular hydrogen bonds have also been characterized for neutral compounds such as methoxyalcohols[15−20] and diols.[16,18,21−27] It has been demonstrated for chloroalkylnitriles that intramolecular solvation stabilizes the transition state of $S_N2$ reactions.[28] Besides mass spectrometric methods, intramolecular solvation has been studied with a variety of other experimental methods such as microwave spectroscopy,[21] gas-phase electron diffraction,[22] and IR,[16] Raman,[23] and NMR[24] spectroscopy.

In the present study, attention was focused on intramolecular solvation of some carboxylate anions. This involves unconventional hydrogen bonds, that is, weak interactions between alkyl hydrogens and nucleophilic centers, $CH^{\delta+}\cdots{}^{-}X$.

Meot-Ner and Deakyne[29] have described unconventional hydrogen bonds. It was shown by using pulsed ionization high-pressure mass spectrometry (PHPMS) that the interaction energies for tetramethylammonium ion clustering onto n-donors such as water, methanol, methylamine, and trimethylamine and with p-donors such as benzene and toluene, range between 8 and 10 kcal/mol. With the weak n-donor methyl chloride, they found the interaction to be even weaker (6.5 kcal/mol). From ab initio calculations, they showed that tetramethylammonium interacts with water, methanol, methylamine, and methyl chloride electrostatically via a cavity created by hydrogens of three methyl groups rather than hydrogen bonding to one hydrogen or to one methyl group. This type of interaction is important in the study of stability and behavior of many biomolecules and could play a decisive role in protein folding.

The basicities of primary *n*-alkylamines[30,31] and the acidities of primary *n*-alkanols[32−34] have been shown to increase monotonically with size. This phenomenon has been explained as due to the occurrence of a coiling effect for compounds containing a linear alkyl group with more than four carbons. The coiling effect results in unconventional hydrogen bonding between the carbon hydrogens and the charge site, thereby providing extra stabilization of the ammonium ion or the alkoxy anion through a polarizability effect.

Catalán[35] has studied the intramolecular solvation of alkoxy anions. By plotting gas-phase acidities as a function of vertical ionization potentials for a homologous series of primary *n*-alkanols, he concluded, from the absence of linearity for alcohols greater than butanol, that these alkoxy anions possess a markedly strained geometry compared to the corresponding neutral form. Catalán further suggested that this phenomenon is the result of intramolecular solvation caused by unconventional hydrogen bonding between the charge site and the carbon hydrogens, $CH^{\delta+}\cdots{}^{-}O$, which he explained as a polarizability effect. However, when gas-phase acidities from a study of collisionally activated metastable ions[36] are used, a linear relationship is observed, which was explained by the fact that the ions under these circumstances possess high effective temperatures[37] and are therefore not expected to undergo intramolecular solvation. For a homologous series of primary *n*-alkylamines, Catalán observed a linear relationship between the gas-phase acidities and the vertical ionization potentials and thus conluded that primary *n*-alkylamines do not undergo intramolecular solvation.

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Caldwell et al.[13] have studied relative gas-phase acidities of various carboxylic acids. They found $\beta$-methylcrotonic acid to be 0.4 kcal/mol less acidic than 3-methylbutyric acid, even though $\beta$-methylcrotonic acid was expected to be more acidic because of the electron-withdrawing field-inductive effect of the vinyl group. They suggested that rotamers of 3-methylbutanoate can be involved in intramolecular hydrogen bonding with the $\gamma$-hydrogens, which will contribute to the stabilization of the anion and thus increase the acidity of 3-methylbutyric acid.

It is our intention in the current work to characterize thermochemically the intramolecular solvation process for some carboxylate anions by the use of PHPMS and ab inito methods.

By use of PHPMS it is possible to measure equilibrium constants for gas-phase ion−molecule reactions as a function of temperature, which effectively leads to a measurement of the enthalpy and entropy changes, eq 1, for the reaction. For proton exchange reactions, such as eq 2, the equilibrium constant, eq 3, can be obtained from the partial pressure ratio between $B_1$ and $B_2$ and the relative abundances of $B_1H^+$ and $B_2H^+$.

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (1)$$

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ \qquad (2)$$

$$K_{eq,2} = \frac{P_{B_1}[B_2H^+]}{P_{B_2}[B_1H^+]} \qquad (3)$$

Examination of the thermochemistry of a reaction is a powerful tool for the inference of gross structural features of an ion. The magnitude of the enthalpy and entropy changes can often be used to give valuable information about the structure of the ion.

When studying equilibrium reactions over an extended temperature range, a curvature in the van't Hoff plot of $\ln K_{eq}$ versus $1/T$ can be observed if one of the participants in the equilibrium can exist in more than one isomeric form, dependent on the temperature. Previous examples[38,39] from this laboratory clearly illustrate how powerful this technique is and how with careful experimental work it has become possible to observe isomeric forms of ionic species in the gas phase relatively frequently using PHPMS.

It has been demonstrated previously that the PHPMS technique can be used to implicate the existence of highly sterically congested structures of adducts derived from the addition of either dimethyl ether or acetone to methylated acetone.[38] It has been demonstrated further that the PHPMS technique can be used to characterize thermochemically the isomerization process of the adduct derived from addition of *tert*-butyl cation to small organic bases such as methanol, ethanol, acetonitrile, dimethyl ether, diethyl ether, and acetone.[39] The two coexisting isomeric forms of the association adduct were identified to be (i) at low-temperature, a covalently bound isomer, $t\text{-}C_4H_9{-}B^+$, characterized by more negative enthalpies and entropies of association and (ii) at higher temperature, an electrostatically bound isomer, $i\text{-}C_4H_8{\cdots}^+HB$, of less negative enthalpies and entropies of association.

Very few cases of direct observation and thermochemical characterization of interconversion of ionic isomers have been reported. Hiraoka and Kebarle[40] observed by use of PHPMS a low-temperature, weakly bound adduct between $C_2H_5^+$ and $H_2$ which overcame a small activation barrier at higher temperature to yield a covalently bound $C_2H_7^+$ species. Sunner et al.[41] also observed a break in the van't Hoff plot for the association reaction between $t\text{-}C_4H_9^+$ and $i\text{-}C_4H_{10}$ which they ascribed to a transition between a tight, covalently bound adduct at low temperature and a "loose", more weakly bound adduct at higher temperature. Bushnell et al.[42] observed, in a high-pressure experiment, a covalent and an electrostatic form of the association adduct between $Sc^+$ and $H_2$. Anicich et al.[43] reported a study of methyl cation clustering onto hydrogen cyanide, in which two isomers were observed, one formed via radiative stabilization, $[CH_3NCH]^+$, and the other by collisional stabilization, $[CH_3CNH]^+$.

Most of the reported thermochemical characterizations of interconversion of ionic isomers have involved isomerization of an association adduct, typically an isomerization between a covalently bound adduct and an electrostatically bound adduct. In this study, the PHPMS technique in conjunction with ab initio methods, was used to characterize thermochemically an intramolecular solvation process involving unconventional hydrogen bonding. The combined experimental and theoretical results are reported herein.

## 2. Experimental Section

**2.1. Equilibrium Measurements.** The equilibrium measurements were made with a pulsed ionization high-pressure mass spectrometer constructed at the University of Waterloo. The apparatus and its capabilities have been described in detail previously.[38]

Gas mixtures were prepared in a temperature-controlled 5 L stainless steel reservoir using methane to a pressure of 950−1200 Torr as the high-pressure bath gas, which served as the inert third body stabilization species. Other components of the mixture were present at pressures of 0.1−2.2 Torr. In addition, 10 Torr of $N_2O$ was added to the mixture in order to generate $O^-$ by dissociative electron capture which subsequently reacted with methane to yield $OH^-$ as the deprotonation chemical ionization reagent ion. The gas mixture was bled into the ion source through a heated stainless steel inlet line to a pressure of ∼4 Torr. Ionization was accomplished by a 300 $\mu$s pulse of 2 keV electrons focused into the ion source through a 150 $\mu$m aperture. The ions diffuse out of the ion source through a second 150 $\mu$m aperture into the source chamber where the pressure is $\leq 100\ \mu$Torr. The ions are then accelerated toward the first cone through a 100−150 V potential drop, where they enter the ion optics region and are accelerated up to 1.2 keV. The signal was monitored by a PC-based multichannel scaler signal acquisition system configured at 10−20 $\mu$s dwell time per channel. A total of 250 channels were acquired using a duty cycle of ∼10 ms greater than the temporal profile for the most persistent ion, which prevents pulse-to-pulse carryover in ion abundance. The results of 1000−3000 electron gun pulses were accumulated, depending on the signal intensity. Representative data are shown in Figure 1 for proton exchange between *n*-decanoate and 2-ethylhexanoate. All materials used were commercial products.

Errors associated with measuring the temperature and the pressure contribute more to the uncertainty in the derived thermochemical data than the actual statistical uncertainty in the van't Hoff plots. These contribute to an estimated experimental uncertainty of ±0.1 kcal/mol for the enthalpy of reaction and ±0.5 cal/mol K for the entropy of reaction.

**2.2. Ab Initio Calculations.** All electronic structure calculations were carried out using the Gaussian 94 suite of programs.[44]

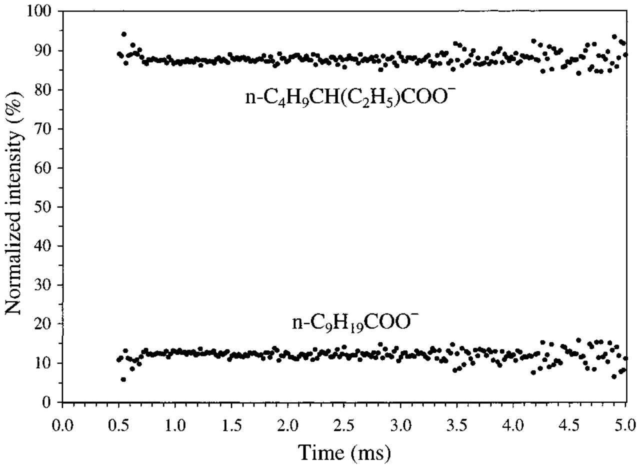


**Figure 1.** Variation of normalized ionic abundance of *n*-decanoate and 2-ethylhexanoate as a function of time after a 300 $\mu$s electron beam pulse. The results of 2000 electron gun pulses were accumulated at an ion source pressure of 4 Torr and an ion source temperature of 563 K (290 °C). Mixture composition: methane (954 Torr), *n*-decanoic acid (130 mTorr), 2-ethylhexanoic acid (260 mTorr).

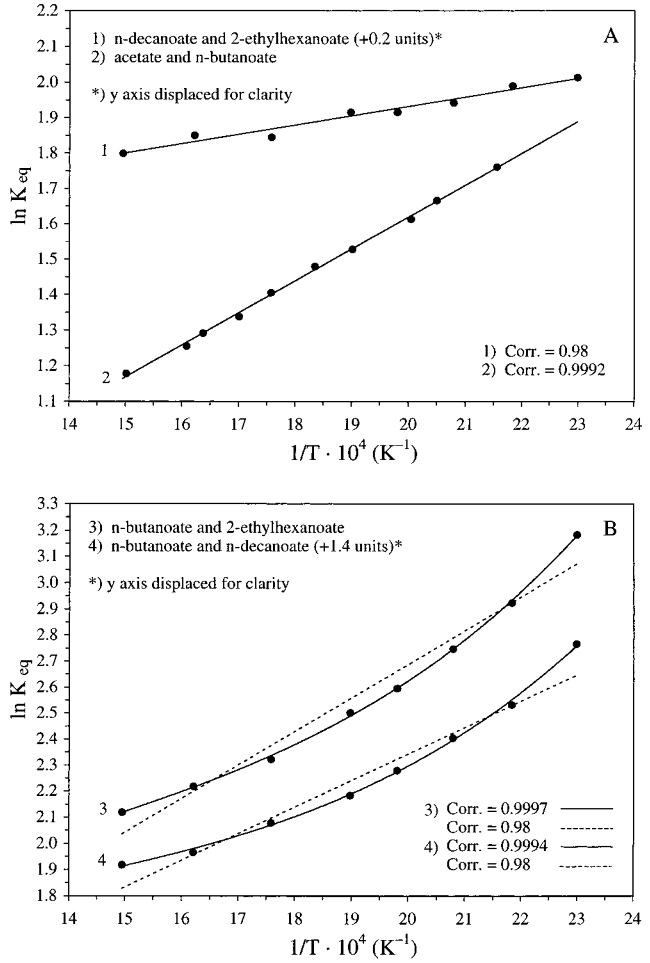


**Figure 2.** Van't Hoff plots for proton exchange between *n*-decanoate and 2-ethylhexanoate (A, 1), acetate and *n*-butanoate (A, 2), *n*-butanoate and 2-ethylhexanoate (B, 3), *n*-butanoate and *n*-decanoate (B, 4).

The thermochemical data (298.15 K) were derived from vibrational frequencies calculated at the HF/6-31+G(d,p) level. Scott and Radom[45] do not report any scaling factors for this method, so the difference between Scott and Radom's[45] reported scaling factors for the HF/6-31G(d) and HF/6-31+G(d) level have been added to the reported scaling factors for the HF/6-31G(d,p) level to give the approximate scaling factors for the HF/6-31+G(d,p) level. The electronic energies and the charges were obtained from single-point calculations at the MP2/6-31+G(d,p) level. The charges were obtained from the natural population analysis (NPA) phase of a natural bond orbital analysis.[46−53]

## 3. Results and Discussion

**3.1. Experimental Results.** The equilibrium constants for proton exchange reactions, eq 4, between various carboxylate anions (acetate, *n*-butanoate, *n*-decanoate, and 2-ethylhexanoate) were measured over an extensive temperature range (parts A and B of Figure 2).

$$R_1COO^- + R_2COOH \rightleftharpoons R_1COOH + R_2COO^- \tag{4}$$

The van't Hoff plot for proton exchange between acetate and *n*-butanoate (Figure 2A) appears linear, which suggests either no isomerization of any of the participants in the equilibrium or that any possible isomerization is thermoneutral or almost thermoneutral. The van't Hoff plots for proton exchange between *n*-butanoate and *n*-decanoate or 2-ethylhexanoate (Figure 2B) show a pronounced curvature, which suggests isomerization of at least one of the participants in the equilibrium. The van't Hoff plot for proton exchange between *n*-decanoate and 2-ethylhexanoate (Figure 2A) appears linear, which, based on the conclusions made from the van't Hoff plots in Figure 2B, suggests almost identical thermochemistry for the isomerization of the participants in the equilibrium.

If it is assumed that the isomerization in question is a conformer change caused by intramolecular solvation, then it is relevant to consider two processes (i) the proton exchange between the two unfolded (no intramolecular solvation) carboxylate anions, eq 5, and (ii) the intramolecular solvation of each of the carboxylate anions, eq 6.

$$R_1COO^-\text{-un} + R_2COOH \rightleftharpoons R_1COOH + R_2COO^-\text{-un} \tag{5}$$

$$R_iCOO^-\text{-un} \rightleftharpoons R_iCOO^-\text{-fo} \tag{6}$$

Since the intramolecular solvation involves weak unconventional hydrogen bonding, it seems reasonable to assume that the neutral carboxylic acids are not involved in intramolecular solvation. For the linear van't Hoff plots, the thermochemical data were extracted using eq 1. To deconvolute the thermochemical data for the processes given by eq 5 and eq 6, the points in the curved van't Hoff plots were fitted with eq 7, where the observed equilibrium constant, $K_{eq,obs}$, is given by eq 8.

$$\ln K_{eq,obs} = \ln\left(\frac{\exp\left(\frac{\Delta S^\circ_{eq,5}}{R} - \frac{\Delta H^\circ_{eq,5}}{RT}\right)\left(1 + \exp\left(\frac{\Delta S^\circ_{eq,6(R_2)}}{R} - \frac{\Delta H^\circ_{eq,6(R_2)}}{RT}\right)\right)}{\left(1 + \exp\left(\frac{\Delta S^\circ_{eq,6(R_1)}}{R} - \frac{\Delta H^\circ_{eq,6(R_1)}}{RT}\right)\right)}\right) \tag{7}$$

$$K_{eq,obs} = \frac{K_{eq,5}(1 + K_{eq,6(R_2)})}{(1 + K_{eq,6(R_1)})} \tag{8}$$

The thermochemical data extracted from the van't Hoff plots in parts A and B of Figure 2 are presented in Table 1.

**TABLE 1: Experimental and Theoretical Δ*H*° and Δ*S*° Values for Proton Exchange, Eq 5, and Intramolecular Solvation, Eq 6, of Carboxylate Anions**

| | | | experimental | | theoretical | |
|---|---|---|---|---|---|---|
| $R_1$ or $R_i$ | $R_2$ or $R_i$ | eq | $\Delta H^{\circ a}$ (kcal/mol) | $\Delta S^{\circ a}$ (cal/mol K) | $\Delta H^{\circ b}$ (kcal/mol) | $\Delta S^{\circ b}$ (cal/mol K) |
| $CH_3$ | *n*-$C_3H_7$ | 4 | −1.8$^{c}$ | −0.4$^{c}$ | | |
| $CH_3$ | *n*-$C_3H_7$-un | 5 | *d* | *d* | −1.0 | −0.2 |
| *n*-$C_3H_7$-un | *n*-$C_9H_{19}$-un | 5 | −0.7 | 1.3 | −0.6 | 1.3 |
| *n*-$C_3H_7$-un | *n*-$C_4H_9CH(C_2H_5)$-un | 5 | −1.1 | 3.9 | *e* | *e* |
| *n*-$C_9H_{19}$ | *n*-$C_4H_9CH(C_2H_5)$ | 4 | −0.5$^{c}$ | 2.4$^{c}$ | | |
| *n*-$C_3H_7$-un | *n*-$C_3H_7$-fo | 6 | 0.0$^{f}$ | 0.1$^{f}$ | −0.7 | −2.5 |
| *n*-$C_9H_{19}$-un | *n*-$C_9H_{19}$-fo | 6 | −7.3 | −17.2 | −3.4 | −8.5 |
| *n*-$C_4H_9CH(C_2H_5)$-un | *n*-$C_4H_9CH(C_2H_5)$-fo | 6 | −7.3 | −16.8 | *e* | *e* |
| *n*-$C_9H_{20}$-un | *n*-$C_9H_{20}$-fo | 10 | *d* | *d* | 2.3 | −1.3 |

[a] Extracted from the van't Hoff plots (Figure 2) using eq 7 unless otherwise noted. [b] From ab initio theory; see text. [c] Extracted from the van't Hoff plot (Figure 2A) using eq 1. [d] Not measured. [e] Not computed. [f] The same values were extracted from both van't Hoff plots (Figure 2B).

Caldwell et al.[13] estimated the reaction enthalpy for the proton transfer between acetate and *n*-butanoate using PHPMS. From a single temperature measurement they obtained the Gibbs free energy for the reaction, assumed the reaction entropy to be negligible, and thus obtained a reaction enthalpy of −2.0 kcal/mol. This value is in excellent agreement with the value of −1.8 kcal/mol measured in this work. The reaction enthalpy for proton exchange corresponds to the proton affinity difference between acetate and *n*-butanoate (acetate having the higher proton affinity) and, also, if the entropy term is disregarded, to the gas-phase acidity difference between acetic acid and *n*-butyric acid (*n*-butyric acid having the higher acidity).

The thermochemical data obtained from the curved van't Hoff plots have been extracted with the assumption that all of the carboxylate anions can be involved in intramolecular solvation. The proton exchange reaction between unfolded *n*-butanoate and unfolded *n*-decanoate is exothermic (−0.7 kcal/mol) and entropically favored (1.3 cal/mol K), which means that *n*-decanoic acid is a stronger acid than *n*-butyric acid and the *n*-butyric acid is, according to the previous discussion, a stronger acid than acetic acid. It appears that an increase of size of the alkyl group is followed by an increase in acidity, which is a rational observation which can be explained from the alkyl group effect.[13] Larger alkyl groups have larger polarizabilities and thus have greater stabilizing effects on the carboxylate anions. The gas-phase acidity for *n*-decanoic acid has not been reported in the literature. To verify that the data for *n*-decanoic acid is realistic, Δ*G*°(600 K) for the proton exchange between acetate and *n*-decanoate (calculated via thermochemical cycles) were plotted (Figure 3) together with data from Caldwell et al.[13] who have measured relative gas-phase acidities for *n*-alkylcarboxylic acids up to *n*-hexanoic acid. The relative gas-phase acidities are plotted versus the number of carbons, *N*, in the alkyl group of the carboxylic acid, $C_NH_{2N+1}COOH$. As is evident from the figure, the acidity increases with increasing size of the alkyl group, which can be attributed to the increase in polarizability and to the intramolecular solvation of the carboxylate anion (which is also linked to the polarizability). These two effects seem, not surprisingly, to have an upper limit, i.e., the relative acidity is seen not to change appreciable after $N = 4$ or 5. The experimental values for *n*-decanoic acid and *n*-butyric acid from this work are to some extent consistent with the trend seen from the data of Caldwell et al.[13]

The proton exchange reaction between unfolded *n*-butanoate and unfolded 2-ethylhexanoate is exothermic (−1.1 kcal/mol) and entropically favored (3.9 cal/mol K), which means that 2-ethylhexanoic acid is a stronger acid than *n*-butyric acid. Since both *n*-decanoic acid and 2-ethylhexanoic acid have been measured relative to *n*-butyric acid, it is possible, via thermochemical cycles, to calculate the enthalpy and entropy of proton exchange between the two carboxylate anions. Doing so, an enthalpy of proton exchange of −0.4 kcal/mol, and an entropy of proton exchange of 2.6 cal/mol K are obtained in favor of protonating *n*-decanoate. These values are in excellent agreement with the values extracted from the linear van't Hoff plot (Figure 2A), which has been derived from direct measurements and which resulted in an enthalpy of proton exchange of −0.5 kcal/mol and an entropy of proton exchange of 2.4 cal/mol K. 2-Ethylhexanoic acid appears to be a stronger acid than *n*-decanoic acid, even though 2-ethylhexanoic acid is smaller in size. This is most likely a branching effect. Branching of the alkyl group has been shown to increase the acidity of alkylcarboxylic acids.[13]

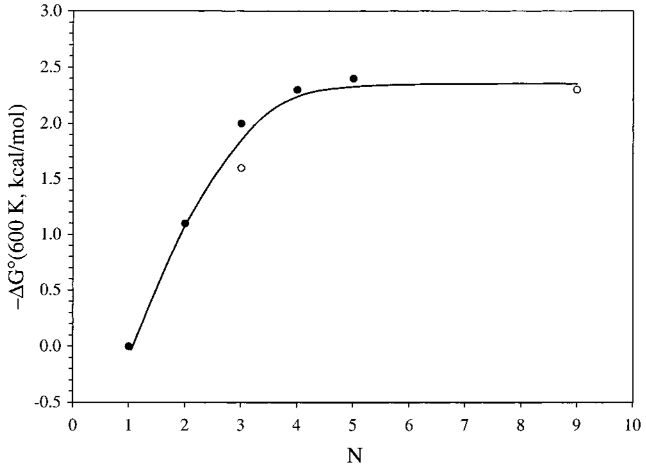
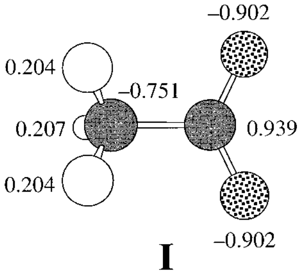


**Figure 3.** Relative (to acetic acid) gas-phase acidities, Δ*G*°(600 K) versus the number of carbons, *N*, in the alkyl group of the carboxylic acid, $C_NH_{2N+1}COOH$. The data are from this work (open data point symbols) and from ref 13 (solid data point symbols): (1) acetic acid; (2) propanoic acid; (3) butanoic acid; (4) pentanoic acid; (5) hexanoic acid; (9) heptanoic acid.

According to both van't Hoff plots in Figure 2B, the enthalpy of intramolecular solvation for *n*-butanoate is 0.0 kcal/mol and the entropy of intramolecular solvation is 0.1 cal/mol K, which suggests that the folding is either nonexistent, thermoneutral, or almost thermoneutral.

For *n*-deacanoate and 2-ethylhexanoate, the enthalpies of intramolecular solvation were measured to each be −7.3 kcal/mol, and the entropies of intramolecular solvation were measured to be −17.2 cal/mol K for *n*-decanoate and −16.8 cal/mol K for 2-ethylhexanoate. Thus, the intramolecular solvation processes for the two carboxylic acids are almost thermochemically identical, which was expected from the linearity of the van't Hoff plot for proton exchange between *n*-decanoate and



**I**

**Figure 4.** Structure of acetate, **I**, calculated at the HF/6-31+G(d,p) level and NPA charges calculated at the MP2/6-31+G(d,p) level.

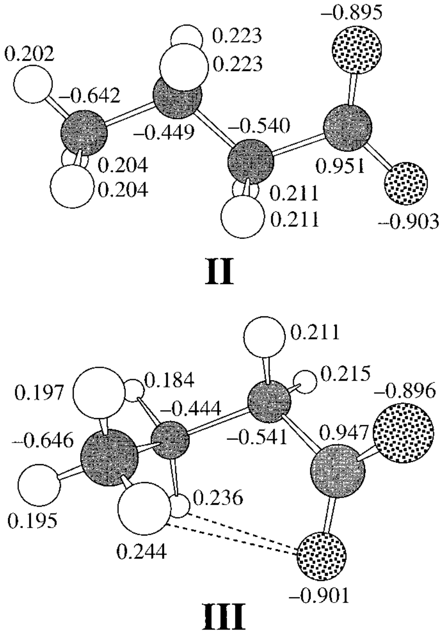


**Figure 5.** Structure of unfolded *n*-butanoate, **II**, and folded *n*-butanoate, **III**, calculated at the HF/6-31+G(d,p) level and NPA charges calculated at the MP2/6-31+G(d,p) level. The dashed lines represent distances less than 3 Å.

2-ethylhexanoate (Figure 2A). The intramolecular solvation processes for *n*-decanoate and 2-ethylhexanoate are exothermic but entropically unfavorable, which is a rational observation for an intramolecular solvation process. The intramolecular solvation results in loss of internal rotors, which will decrease the entropy change for the reaction and thus make the intramolecular solvation entropically unfavorable. The complexity of the folding process for these large systems, and the fact that unconventional hydrogen bonding is involved, has made it impossible to compare the enthalpy of intramolecular solvation to any literature values. Since the entropy of intramolecular solvation results in loss of internal rotors, it makes sense to compare this property with the few literature values that exist. Szulejko et al.[14] have studied the thermochemistry of the intramolecular solvation process for protonated $\omega$-methoxyalkanols and found for the largest system studied (5-methoxypentanol) an entropy of intramolecular solvation of −18.5 cal/mol K. This is a crude comparison and can therefore only be used to indicate whether the values from this work (−17.2 and −16.8 cal/mol K) are in a realistic range, which they clearly appear to be.

**3.2. Theoretical Results.** Ab initio calculations were employed in order to support the experimental thermochemical data and the conclusions derived from these.

Structures for unfolded conformers of acetic acid, *n*-butyric acid, and *n*-decanoic acid were calculated. The corresponding unfolded conformers of the carboxylate anions were calculated as well (Figures 4−6, **I**, **II**, **IV**), along with suggested structures of the folded (intramolecular solvated) conformers (Figures 5 and 6, **III**, **V**).

In Figure 4, the structure of acetate, **I**, is shown, which corresponds energetically to the global minimum. Acetate is the only carboxylate studied which cannot be folded. Since the intramolecular solvation involves unconventional hydrogen bonding, which involves electrostatic ion dipole and ion-induced dipole interactions, it is reasonable to consider the charge distribution within the carboxylate anions.

In Figure 5, the unfolded conformer, **II**, and a suggested folded conformer, **III**, of *n*-butanoate are shown. Whether or not a folded or an unfolded conformer is considered, the partially positively charged α-hydrogens will always be in close proximity to the partially negatively charged oxygens, so a conformer change will result in either an insignificant change in the interaction between the α-hydrogens and the oxygens or no change at all. Therefore, no reason exists to consider the α-hydrogens in the discussion. Different conformers are associated with different energies, i.e., the relative energy for a particular conformer is determined by the net result of the intramolecular repulsions, e.g., between hydrogens, and the intramolecular attractions, e.g., between hydrogens and oxygens. The folded conformer of *n*-butanoate, **III**, is lower in energy than the unfolded conformer, **II**. From the figure, it is evident that one $\beta$- and one $\gamma$-hydrogen are in close proximity to one of the oxygens (indicated by the dashed lines). These endo hydrogens have charges which are 25−30% higher than the charges on the exo hydrogens, which indicates an interaction between the endo hydrogens and one of the oxygens. The alkyl group has been locally polarized, and the original dipole moment has been increased because of the close proximity of the negatively charged oxygen. These interactions are not present (or at least not to the same extent) in the unfolded conformer. These additional (relative to the unfolded conformer) interactions provide the ion with additional stabilization, which in mathematical terms can be expressed in the following way:[54]

$$E_{\mathrm{stab}} = -\frac{\alpha q^2}{2r^4} \tag{9}$$

$E_{\mathrm{stab}}$ is the stabilization energy, α the polarizability, *q* the charge, and *r* the distance between the polarizable group and the charge site. These additional intramolecular interactions are what constitute the intramolecular solvation for the systems studied.

In Figure 6, the unfolded conformer, **IV**, and one possible folded conformer, **V**, of *n*-decanoate are shown. The long alkyl group in this system permits unconventional hydrogen bonding at several sites, and should make the intramolecular solvation even more (relative to *n*-butanoate) exothermic, which is indeed observed. In this system the polarizability effect on the hydrogens is very distinct in the folded conformer, **V**. As is evident from Figure 6, the hydrogens more or less form a cavity around one of the oxygens. The extent of polarization is determined by the magnitude of the charge (*q* in eq 9) and the distance between the polarizable group and the charge site (*r* in eq 9), so the closer the hydrogens are to the oxygen, the more they are polarized. In the folded conformer of *n*-decanoate, **V**, the endo hydrogens have between 12 and 40% higher charges compared to the exo hydrogens.

Another way to illustrate this polarizability effect is to consider the two conformers of *n*-decanoate, **IV** and **V**, where

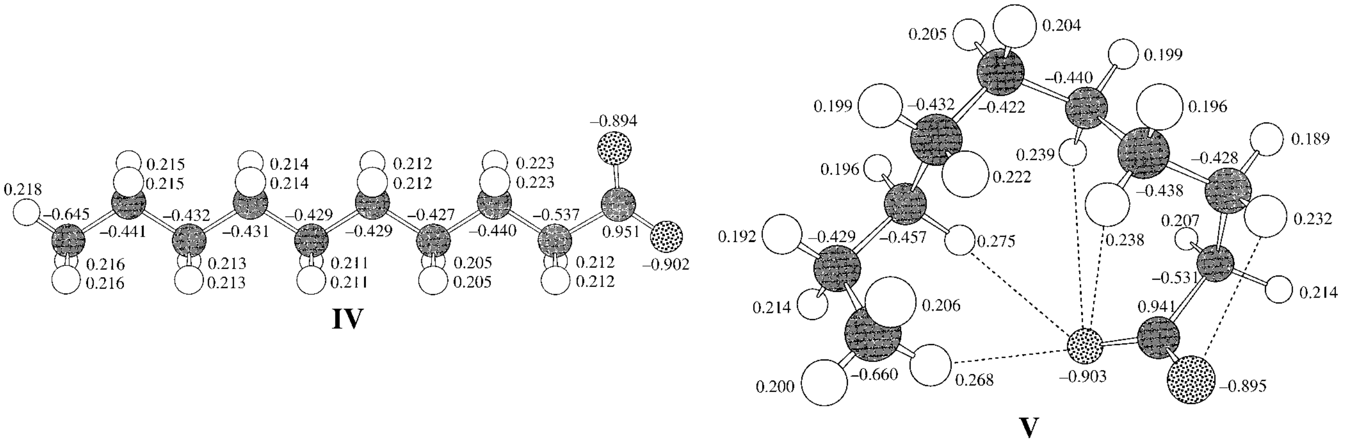


**Figure 6.** Structure of unfolded *n*-decanoate, **IV**, and folded *n*-decanoate, **V**, calculated at the HF/6-31+G(d,p) level and NPA charges calculated at the MP2/6-31+G(d,p) level. The dashed lines represent distances less than 3 Å.

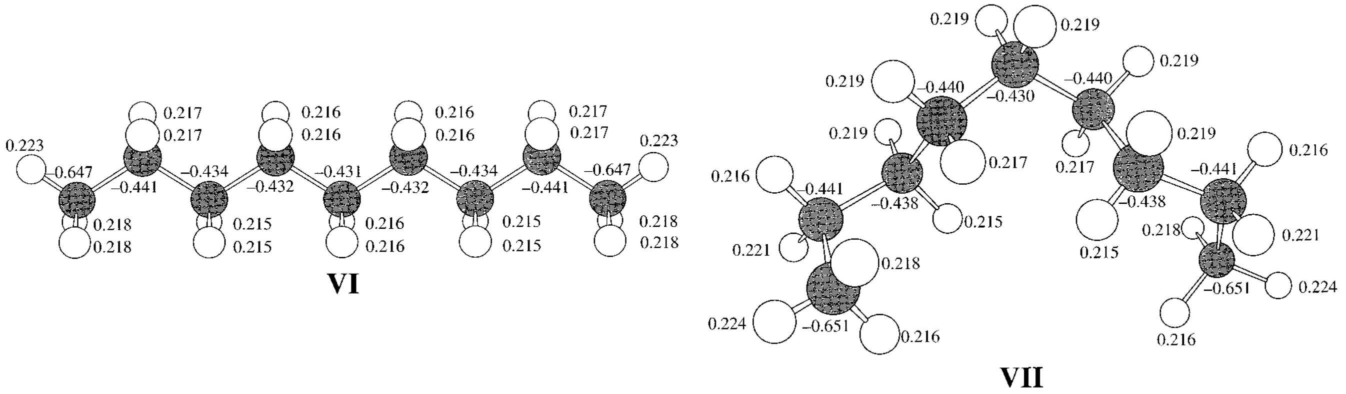


**Figure 7.** Structure of unfolded *n*-nonane, **VI**, and folded *n*-nonane, **VII**, calculated at the HF/6-31+G(d,p) level and NPA charges calculated at the MP2/6-31+G(d,p) level.

the carboxylate group has been substituted by a hydrogen. This corresponds to *n*-nonane. In Figure 7, the two analogous (relative to *n*-decanoate) conformers of *n*-nonane are shown, an unfolded conformer, **VI**, and a folded conformer, **VII**. From the figure it is evident that the polarization present in the folded conformer of *n*-decanoate, **V**, is absent in the folded conformer of *n*-nonane, **VII**. The difference in charge distribution in the alkyl group illustrates the polarizibility effect caused by the carboxylate group. From the unfolded conformer of *n*-nonane, **VI**, it can be seen that the charge distribution is, not surprisingly, symmetrically distributed. In the folded form of *n*-nonane, **VII**; however, the charge is distributed somewhat less symmetrically. This is because the partial charges on the molecule are interacting with other parts of the molecule, and since the folded conformer of *n*-nonane, **VII**, contains less symmetry than the unfolded conformer, **VI**, it will have a less symmetrical distribution of charges. If the same (as for the folded conformer of *n*-decanoate) inner and exo hydrogens are considered in the folded conformer of *n*-nonane, **VII**, it can be seen from the charges that the exo hydrogens now have 1−3% higher charges than the endo hydrogens. This opposite effect can be explained by the fact that all the endo hydrogens are in fairly close proximity to each other, such that they constitute a cavity of partial positive charge, which will then transfer positive charge to the exo hydrogens, to reduce the repulsion energy between the endo hydrogens.

Thermochemical data for proton exchange between the unfolded conformers, eq 5, of acetate, *n*-butanoate, and *n*-decanoate were also calculated and are shown in Table 1.

The enthalpy and entropy of proton exchange between unfolded *n*-butanoate and unfolded *n*-decanoate were calculated to be −0.6 kcal/mol and 1.3 cal/mol K respectively, in excellent agreement with the experimental values of −0.7 kcal/mol and 1.3 cal/mol K. This indicates that the theoretical method is reliable for the systems studied.

The enthalpy and entropy of proton exchange between acetate and unfolded *n*-butanoate were calculated to be −1.0 kcal/mol and −0.2 cal/mol K. The calculated enthalpy of proton exchange seems to be in poor agreement with the experimental value of −1.8 kcal/mol, which was extracted from a linear van't Hoff plot (Figure 2A), i.e., by neglecting the contribution from a possible folded conformer of *n*-butanoate. The existence of a folded conformer of *n*-butanoate has, according to previous discussion, been verified. So the fact that the experimental enthalpy of proton exchange is more negative than the calculated value suggests that there is a contribution from the folded conformer of *n*-butanoate in the temperature range studied. Since the van't Hoff plot appears to be linear, the relative amounts of folded and unfolded *n*-butanoate do not change significantly over the temperature range studied since the free energy does not change significantly. Consistent with this, the ab initio data calculate a change in composition of only 7% between 435 and 66 K (see Table 2). The experimental data (Table 1) would give an even smaller change. The experimentally determined entropy of proton exchange between acetate and unfolded *n*-butanoate (−0.4 cal/mol K) suggests however that there is no contribution from a folded conformer of *n*-butanoate.

Thermochemical data for intramolecular solvation, eq 6, of *n*-butanoate and *n*-decanoate were calculated and are given in Table 1.

The enthalpy and entropy of intramolecular solvation of *n*-butanoate were calculated to be −0.7 kcal/mol and −2.5 cal/

**TABLE 2: Calculated Composition,[a] Eq 11, for the Coexisting Conformers, Eq 6, of the Carboxylate Anions at the Highest and Lowest Temperature Studied**

| | | 435 K | | 669 K | |
|---|---|---|---|---|---|
| $R_i$ | $T_{50\%}$[b] (K) | unfolded (%) | folded (%) | unfolded (%) | folded (%) |
| $n$-$C_3H_7$ | 280[c] | 61[c] | 39[c] | 68[c] | 32[c] |
| $n$-$C_9H_{19}$ | 424 | 55 | 45 | 96 | 4 |
| $n$-$C_4H_9CH(C_2H_5)$ | 435 | 50 | 50 | 95 | 5 |

[a] Calculated from the experimental results unless otherwise noted. [b] The temperature for which there is 50% of each conformer ($\Delta G° = 0$ kcal/mol). [c] Calculated from the theoretical results.

mol K. As expected, according to previous discussion, the intramolecular solvation for $n$-butanoate is almost thermoneutral. A value of −0.7 kcal/mol will result in a curvature in the van't Hoff plot so subtle that it will be impossible to observe because of the scatter of the points. It is therefore not surprising that the van't Hoff plot (Figure 2A) appears linear in the temperature range studied. The experimental enthalpy and entropy of intramolecular solvation for $n$-butanoate (0.0 kcal/mol and 0.1 cal/mol K) are not in good agreement with the calculated values. Since the theoretical method has proven to be reliable in other cases, the experimental values are likely in error. This is not unreasonable since the fitting procedure used for curved van't Hoff plots is not readily applicable for processes which are thermoneutral or nearly thermoneutral.

The enthalpy and entropy of intramolecular solvation of $n$-decanoate were calculated to be −3.4 kcal/mol and −8.5 cal/mol K. By increasing the size of the $n$-alkyl group, the number of ways in which the group can fold around the charge site will increase significantly. For $n$-decanoate, there are so many possible folded conformers that it would be naive to assume that the suggested folded conformer of $n$-decanoate, **V**, in Figure 6 energetically corresponds to the global minimum. If the suggested folded conformer of $n$-decanoate, **V**, corresponds to a local minimum, then the calculated enthalpy and entropy of intramolecular solvation should be less negative than the experimental values, which is clearly the case; see Table 1. The experimental values for enthalpy and entropy of intramolecular solvation for $n$-decanoate (−7.3 kcal/mol and −17.2 cal/mol K) are most likely average values of several conformers characterized by similar thermochemistry.

To illustrate further that the folding process for $n$-decanoate is exothermic because of the unconventional hydrogen bonding, the thermochemical data for the corresponding folding process for $n$-nonane, eq 10, was calculated.

$$n\text{-}C_9H_{20}\text{-un} \rightleftharpoons n\text{-}C_9H_{20}\text{-fo} \qquad (10)$$

As expected, the folding process, eq 10, was found to be endothermic (2.3 kcal/mol) and entropically unfavorable (−1.3 cal/mol K), which supports the fact that it is the carboxylate group in folded $n$-decanoate which interacts (via the negatively charged oxygens) with the alkyl group, thus providing the extra stabilization which makes the folding process exothermic. Since the folding process for $n$-nonane, eq 10, is endothermic and entropically unfavorable, the process will be endoergic at all temperatures.

From the enthalpy and entropy of intramolecular solvation, eq 6, an equilibrium constant, $K_{eq,6}$, for a given temperature can be calculated from eq 1, which can be used to calculate the composition, eq 11, for the coexisting conformers of the carboxylate anions at a given temperature.

$$[R_iCOO^-\text{-fo}] = \frac{100\%}{1 + 1/K_{eq,6}} \qquad (11)$$

This was done for $n$-butanoate, $n$-decanoate, and 2-ethylhexanoate for the highest and lowest temperatures studied; see Table 2. Since the thermochemical values for the intramolecular solvation with respect to $n$-decanoate and 2-ethylhexanoate most likely are based on an average of multiple conformers of the intramolcular solvated form, the compositions will therefore also be average values.

The thermochemical values for the intramolecular solvation for $n$-decanoate and 2-ethylhexanoate are almost identical, so the composition for these two systems will therefore also be similar. There are approximately equal amounts of each conformer for both $n$-decanoate and 2-ethylhexanoate at the lowest temperature studied and almost exclusively the unfolded conformer for both systems at the highest temperature studied; see Table 2.

The conformer composition of $n$-butanoate is, as expected according to previous discussion, fairly unchanged over the temperature range studied. At 435 K, there is 39% of the folded conformer of $n$-butanoate, and at 669 K there is 32%. This is only a 7% change over a temperature range of 234 K.

The temperature for which there will be equal amounts of the unfolded and folded carboxylate conformer (if only one folded conformer is assumed) is the temperature, $T_{50\%}$, for which the Gibbs free energy for the intramolecular solvation is zero. These temperatures were calculated for $n$-butanoate, $n$-decanoate, and 2-ethylhexanoate; see Table 2. The curvature in a van't Hoff plot where one of the participants is involved in intramolecular solvation will be most pronounced at $T_{50\%}$. In this sense, the temperature range studied is almost perfect with respect to $n$-decanoate and 2-ethylhexanoate, in that the lowest temperature studied is very close to $T_{50\%}$. For $n$-butanoate, $T_{50\%} = 280$ K, which is out of the temperature range of the instrument used. This further explains why it was not possible to observe clearly the curvature in the van't Hoff plot for proton exchange between acetate and $n$-butanoate (Figure 2A).

The magnitude of $T_{50\%}$ is determined by a combination of the enthalpy and entropy of intramolecular solvation. The lower the enthalpy of intramolecular solvation is, compared to the entropy of intramolecular solvation, the lower $T_{50\%}$. The enthalpy term increases more drastically than the entropy term for an increasing size of the carboxylate, so $T_{50\%}$ will be higher for larger systems. The enthalpy of intramolecular solvation for $n$-alkylcarboxylates is determined by several factors. The larger the size of the alkyl group, the more polarizable it is and the more favorably it will interact with the charge site. The larger the size of the alkyl group, the greater the number of unconventional hydrogen bonds that can be formed. At some point though, there will not be any more space available around the charge site, so the effect will not increase further with size. Larger carboxylates are therefore characterized by more negative enthalpies for intramolecular solvation up to a point where the effect levels off. The entropy of intramolecular solvation is determined by the extent of folding (the more folded the more internal rotors will be lost) and the more unfavorable entropy of intramolecular solvation. As discussed previously, the extent of folding is determined by the size, so larger carboxylates are therefore characterized with more negative entropies for intramolecular solvation up to a point where the effect will level off. In summary, larger $n$-alkylcarboxylates are characterized with more negative enthalpies and entropies of intramolecular solvation, more significant temperature dependence with respect to the conformer composition, and higher $T_{50\%}$ values. These properties will level off fairly rapidly with increasing size of the *n*-alkylcarboxylate. The two largest systems, 2-ethylhexanoate and *n*-decanoate, are similar in size and thus have almost identical thermochemistry.

The increase in gas-phase acidity for an increasing size of the alkyl group is often attributed to the increase in polarizability of the alkyl group, which will increase the stabilization of the carboxylate anion because of the inductive effect, and thus increase the gas phase acidity. We have, in this work, shown that intramolecular solvation also plays an important role in the stabilazation of carboxylate anions, and thus in the gas-phase acidity. The two effects are both linked to the polarizability of the alkyl group. Since especially the large carboxylates are characterized with a significant entropy of intramolecular solvation, which will be manifested in the thermochemistry of proton exchange reactions, the general approximation of neglecting the entropy term for proton exchange reactions is not valid especially for large carboxylic acids.

## 4. Conclusion

Proton exchange reactions between acetate, *n*-butanoate, 2-ethylhexanoate, and *n*-decanoate were studied experimentally by PHPMS and theoretically by ab initio methods.

The van't Hoff plots for proton exchange between *n*-butanoate and *n*-decanoate or 2-ethylhexanoate have a curvature, which suggests isomerization of at least one of the participants in the equilibrium. This isomerization is suggested to be an intramolecular solvation of the carboxylate anions via unconventional hydrogen bonding.

An ab initio study of some folded and unfolded conformers showed that the alkyl group in the folded conformer of the carboxylate anion interacts with the negatively charged oxygens. This interaction (the unconventional hydrogen bond) is manifested in the charge distribution of the alkyl group, which clearly shows that the alkyl group is being polarized at several sites by the negatively charged oxygen, creating an extra stabilization of the carboxylate anion, which in turn will affect the physical properties of the ion.

Thermochemical values for the intramolecular solvation were deconvoluted from the curved van't Hoff plots by a fitting procedure. The enthalpy and entropy of intramolecular solvation for *n*-decanoate were found to be −7.3 kcal/mol and −17.2 cal/mol K, and −7.3 kcal/mol and −16.8 cal/mol K for 2-ethylhexanoate. The fitting procedure proved to be insufficient for processes involving isomerizations which are close to thermoneutral. The calculated values have therefore been adopted for *n*-butanoate, which was found to be −0.7 kcal/mol and −2.5 cal/mol K.

The thermochemistry for the intramolecular solvation was used to derive various properties associated with the process. Larger *n*-alkylcarboxylates are characterized by more negative enthalpies and entropies of intramolecular solvation, more significant temperature dependence with respect to the conformer composition and higher $T_{50\%}$ values (the temperature for which there is 50% of each conformer). These properties level off fairly rapidly with increasing size of the *n*-alkylcarboxylate. The two largest systems studied, 2-ethylhexanoate and *n*-decanoate, are similar in size and thus have almost identical thermochemistry.

We have therefore shown that intramolecular solvation plays an important role in the stabilazation of carboxylate anions, and thus in the gas-phase acidity. Since the large carboxylates are characterized with a significant entropy of intramolecular solvation, which will be manifested in the thermochemistry of proton exchange reactions, the general approximation of neglecting the entropy term for proton exchange reactions is not valid for particularly large carboxylic acids.

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**Supporting Information Available:** MP2/6-31+G(d,p) total energies (Table S1) and archive entries for the HF/6-31+G(d,p) optimized geometries (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Crupi, V.; Jannelli, M. P.; Magazu, S.; Maisano, G.; Majolino, D.; Migliardo, P.; Sirna, D. *Mol. Phys.* **1995**, *84*, 645.

(2) Singelenberg, F. A. J.; Lutz, E. T. G.; van der Maas, J. H.; Jalsovszky, G. *J. Mol. Struct.* **1991**, *245*, 173.

(3) Chen, Q.-F.; Stone, J. A. *J. Phys. Chem.* **1995**, *99*, 1442.

(4) Winkler, F. J.; Stahl, D. *J. Am. Chem. Soc.* **1979**, *101*, 3685.

(5) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504.

(6) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393.

(7) Yamabe, S.; Hirao, K.; Wasada, H. *J. Phys. Chem.* **1992**, *96*, 10261.

(8) Weinkam, R. J. *Biomed. Mass Spectrom.* **1978**, *5*, 334.

(9) Meot-Ner, M. *J. Am. Chem. Soc.* **1983**, *105*, 4906.

(10) Bouchoux, G.; Hoppilliard, Y.; Houriet, R. *New J. Chem.* **1987**, *11*, 225.

(11) Meot-Ner, M. *J. Am. Chem. Soc.* **1984**, *106*, 278.

(12) Lau, Y. K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 7328.

(13) Caldwell, G.; Renneboog, R.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 611.

(14) Szulejko, J. E.; McMahon, T. B.; Troude, V.; Bouchoux, G.; Audier, H. E. *J. Phys. Chem. A* **1998**, *102*, 1879.

(15) Buckeley, P.; Brochu, M. *Can. J. Chem.* **1972**, *50*, 1149.

(16) Singelenberg, F. A. J.; van der Maas, J. H. *J. Mol. Struct.* **1991**, *243*, 111.

(17) Vasquez, S.; Mosquera, R. A.; Rios, M. A.; van Alsenoy, C. *J. Mol. Struct. (THEOCHEM)* **1982**, *188*, 95.

(18) Lii, J. H.; Allinger, N. L. *J. Phys. Org. Chem.* **1994**, *7*, 591.

(19) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1989**, *43*, 715.

(20) Murcko, M. A.; Dilaola, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 10010.

(21) Caminati, W.; Melandri, S.; Favero, P. G. *J. Mol. Struct.* **1995**, *171*, 394.

(22) Kinneging, A. J.; Mom, V.; Mijhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1982**, *82*, 271.

(23) Shagidullin, R. R.; Chernova, A. V. *Russ. Chem. Bull.* **1993**, *42*, 1505.

(24) Abe, A.; Inomata, K. *J. Mol. Struct.* **1991**, *245*, 399.

(25) Chidichimo, G.; Imbardelli, D.; Longeri, M.; Saupe, A. *Mol. Phys.* **1988**, *65*, 1143.

(26) Reiling, S.; Brickmann, J.; Schlenkrich, M.; Bopp, P. A. *J. Comput. Chem.* **1996**, *17*, 133.

(27) Vasquez, S. A.; Rios, M. A.; Carballeira, L. *J. Comput. Chem.* **1992**, *13*, 851.

(28) Craig, S. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1996**, *118*, 6786.

(29) Meot-Ner, M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 469.

(30) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311.

(31) Aue, D. H.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9, p 1.

(32) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046, 6056.

(33) Bartmess, J. E.; McIver, R. T., Jr. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11, p 87.

(34) Boand, G.; Houriet, R.; Gauman, T. *J. Am. Chem. Soc.* **1970**, *90*, 6561.

(35) Catalán, J. *Chem. Phys. Lett.* **1994**, *221*, 68.

(36) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973.

(37) Vékey, K. *J. Mass Spectrom.* **1996**, *31*, 445.

(38) Szulejko, J. E.; Fisher, J. J.; McMahon, T. B.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 147.

(39) Norrman, K.; McMahon, T. B. *J. Am. Chem. Soc.* **1996**, *118*, 2449.

(40) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

(41) Sunner, J. A.; Hirao, K.; Kebarle, P. *J. Phys. Chem.* **1989**, *93*, 4010.

(42) Bushnell, J. E.; Kemper, P. R.; Maitre, P.; Bowers, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 9710.

(43) Anicich, V. G.; Sen, A. D.; Huntress, W. T., Jr.; McEwan, M. J. *J. Chem. Phys.* **1995**, *102*, 3256.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(45) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(46) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.

(47) Carpenter, J. E. Ph.D. Thesis, University of Wisconsin, 1987.

(48) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(49) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

(50) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 1736.

(51) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(52) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(53) Weinhold, F.; Carpenter, J. E. *The Structure of Small Molecules and Ions*; Plenum: New York, 1988.

(54) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1968**, *90*, 6561.