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# CARBOXYLIC ACIDS IN DIMETHYLSULFOXIDE. A CALORIMETRIC STUDY

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## ABSTRACT

Calorimetric data are presented for the solution and ionization of carboxylic acids in dimethylsulfoxide. The compounds studied include acetic acid and its trifluoro-, dichloro- and monochloro-derivatives, and benzoic acids and its 2-nitro- and 3,5-dinitro-derivatives. Ionization of the substituted acetic acids is increasingly endothermic from $CF_3CO_2H$ (+1.8 kJ mol$^{-1}$) to $CHCl_2CO_2H$ (+17.6 kJ mol$^{-1}$), $CH_2ClCO_2H$ (+32.2 kJ mol$^{-1}$), and $CH_3CO_2H$ (+44.8 kJ mol$^{-1}$). A useful linear correlation is found between the enthalpy and free energy of ionization of the acids. The hydrogen bond energy for the hydrogendiacetate ion is estimated as −115 kJ mol$^{-1}$.

## INTRODUCTION

We have been studying the protonation of bases B [1] and the ionization of acids AH [2] in dimethylsulfoxide ($Me_2SO$), a widely used basic, dipolar aprotic solvent. Our aim is to compare the thermodynamics of both processes in $Me_2SO$ and water, and to interpret the data in terms of enthalpy and free energy of transfer, between both solvents, for the solutes B, AH, $BH^+$, $A^-$, and $H^+$ [2]. Such transfer parameters, the enthalpies in particular, can then be rationalized on the basis of properties of the solutes and solvents.

Carboxylic acids constitute an important class of acids. These acids, as are other uncharged acids, are much weaker in $Me_2SO$ than in water, mainly because of the much poorer solvation of the anion $A^-$ in $Me_2SO$ which has no H-bond donor properties. While $pK_a$ values for the ionization of carboxylic acids in $Me_2SO$ have been reported [3,4,5], only a few of the corresponding enthalpies of ionization are available [6].

We present here calorimetric data for the solution and ionization in $Me_2SO$ at 25°C of seven carboxylic acids: $CF_3CO_2H$, $CHCl_2CO_2H$, $CH_2ClCO_2H$, $CH_3CO_2H$, plus benzoic acid and its 2-nitro- and 3,5-dinitro-derivatives. The ionization enthalpies of the acids show a useful linear

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correlation with their p$K_a$ values and our data are also used to estimate the H-bond energy for the $H(CH_3CO_2)_2^-$ ion.

## EXPERIMENTAL

### Materials

The sources of the carboxylic acids and their purity as determined by acidimetric titration were as follows: $CF_3CO_2H$ (Baker, 99.7 ± 0.1%), $CHCl_2CO_2H$ (Fisher, 99.6 ± 0.1%), $CH_2ClCO_2H$ (Fisher, 99.6 ± 0.1%), $CH_3CO_2H$ (Fisher, 99.6 ± 0.2%), benzoic acid (McArthur, 100.1 ± 0.5%), 2-nitrobenzoic acid (Baker, 'Baker grade'), 3,5-dinitrobenzoic acid (Fisher 99.8 ± 0.2%). Tetraethylammonium acetate tetrahydrate (Eastman) was dried under vacuum for 48 h at 40 °C (to avoid decomposition) and then contained 1.0% water. Dimethylsulfoxide (Fisher, Spectroanalyzed) was treated with 4A molecular sieves and, after decantation, distilled under vacuum. Dimethylsulfoxide (Anachemia) was used as received.

### Calorimetric measurements

The calorimetric measurements were made at 25.00 ± 0.01 °C with an LKB Model 8725-2 isoperibol calorimeter essentially as described previously [7], using both the 25 ml and 100 ml cells. The amount of acid dissolved in the various $Me_2SO$ solutions was deduced from the weights of the glass ampoules.

## RESULTS

### Solution enthalpies

The values of the heats of solution of liquid (l) or solid (c) acids were plotted against the number of moles of acids dissolved. The linear relations obtained confirm that in $Me_2SO$, a basic solvent, self-association of the carboxylic acid is negligible at least up to 0.40 M, the maximum concentration used here. This result, which is in agreement with $^1H$ NMR data [8], comes as no surprise since we have already shown that $CH_3CO_2H$ is also a monomer below 0.4 M in sulfolane [9], even though this latter solvent is less basic than $Me_2SO$. The possible effect of the ionization of the acids AH on their heats of solution was also considered. For the strongest acid studied here, $CF_3CO_2H$, with p$K_a$ = 3.45 [10], and at the lowest concentration used, the ionized fraction is 8%. However, the corresponding ionization correction is negligible because, as we shall see, the enthalpy of ionization (+1.8 kJ

TABLE 1

Solution enthalpies (kJ $mol^{-1}$) of carboxylic acids in $Me_2SO$, $\Delta H_s^{\ominus}$, at 25 °C

| Acid | $\Delta H_s^{\ominus}$ | Acid | $\Delta H_s^{\ominus}$ |
|---|---|---|---|
| $CF_3CO_2H$(l) | $-25.6$ | $C_6H_5CO_2H$(c) | $+5.3$ [a] |
| $CHCl_2CO_2H$(l) | $-25.6$ | 2-Nitrobenzoic(c) | $+4.7$ |
| $CH_2ClCO_2H$(c) | $-1.2$ | 3,5-Dinitrobenzoic(c) | $+3.8$ |
| $CH_3CO_2H$(l) | $-8.4$ | | |

[a] Value from ref. 6.

$mol^{-1}$) is much smaller than the enthalpy of solution ($-25.6$ kJ $mol^{-1}$). We can therefore conclude that the slopes of the least-square lines, giving the heats of solution of the acids against the number of moles dissolved, correspond to $\Delta H_s$, the molar enthalpy of solution for reaction (1)

$$AH(1 \text{ or } c) = AH(s) \tag{1}$$

The values of $\Delta H_s$, which can be approximated to $\Delta H_s^{\ominus}$, are given in Table 1.

## *Ionization enthalpies*

We used two different thermochemical cycles to obtain the ionization enthalpies $\Delta H_i$ corresponding to reaction (2)

$$AH(s) = A^-(s) + H^+(s) \tag{2}$$

The first thermochemical cycle involves the determination of $\Delta H_3$, the enthalpy of solution of the acid in a 0.05 M solution of a base B according to reaction (3)

$$AH(1 \text{ or } c) + B(s) = A^-(s) + BH^+(s) \tag{3}$$

The values of the heat of solution were plotted against the number of moles of acid dissolved, and the slope of the least-square line gave $\Delta H_3$. This value was combined with $\Delta H_s$ and with $\Delta H_4$, the known enthalpy of protonation of B, determined using the strong acid $CF_3SO_3H$ [10]

$$H^+(s) + B(s) = BH^+(s) \tag{4}$$

We thus obtained $\Delta H_i$ for reaction (2) as

$$\Delta H_i = \Delta H_3 - \Delta H_s - \Delta H_4 \tag{5}$$

This method was used to determine $\Delta H_i$ for the acids $CF_3CO_2H$, $CH_3CO_2H$, and $C_6H_5CO_2H$. The bases B were 4-amino-2,6-dimethylpyrimidine (Dap) ($pK_a(BH^+) = 6.38$ [1]) for $CF_3CO_2H$, and a stronger base, tetramethylguanidine (TMG) ($pK_a(BH^+) = 13.4$ [4,11]) for the weaker acids $CH_3CO_2H$ and $C_6H_5CO_2H$. The protonation enthalpies $\Delta H_4$ of Dap and TMG were taken as $-42.4 \pm 0.4$ kJ $mol^{-1}$ and $-85.8 \pm 0.4$ kJ $mol^{-1}$ respectively [1,12].

The second thermochemical cycle used is based on the formation of the stable hydrogendiacetate anion according to reaction (6)

$$HA(l \text{ or } c) + 2\ CH_3CO_2^-(s) = H(CH_3CO_2)_2^-(s) + A^-(s) \qquad (6)$$

The heats of solution of the acids in a 0.2 M solution of tetraethylammonium acetate were plotted against the number of moles of acid dissolved and the slope of the least-square lines gave $\Delta H_6$ for reaction (6). We then combined $\Delta H_5$ and $\Delta H_s$, the enthalpy of solution of HA for reaction (1), to yield $\Delta H_7$ for reaction (7).

$$HA(s) + 2\ CH_3CO_2^-(s) = H(CH_3CO_2)_2^-(s) + A^-(s) \qquad (7)$$

We had previously determined [13] the enthalpy for reaction (8), using $CF_3SO_3H$, as $\Delta H_8 = -59.4$ kJ mol$^{-1}$

$$H^+(s) + 2\ CH_3CO_2^-(s) = H(CH_3CO_2)_2^-(s) \qquad (8)$$

Combining $\Delta H_8$ and $\Delta H_7$ led to the desired ionization enthalpy $\Delta H_i$ for reaction (2).

The form in which reaction (6) is written implies that the formation of symmetrical $H(CH_3CO_2)_2^-$ is favored over that of unsymmetrical anions such as $(CF_3CO_2)H(CH_3CO_2)^-$. The formation constants of the anions indicate that this is the case [13]. The proportionality between the heat evolved, when dissolving HA in 0.2 M $NEt_4CH_3CO_2$ (a large excess), and the number of moles of HA dissolved is also in favor of our assumption. Finally, the good agreement between the values of $\Delta H_i$ for $CF_3CO_2H$, $CH_3CO_2H$, and $C_6H_5CO_2H$ obtained using the two thermochemical cycles provides added support. Values of $\Delta H_i$ were obtained through the hydrogendiacetate cycle for all acids except $C_6H_5CO_2H$. The $\Delta H_i$ values which

TABLE 2

Ionization constants, p$K_a$ and enthalpies of ionization of carboxylic acids in $Me_2SO$, $\Delta H_i^\ominus$, at 25 °C and enthalpies of deprotonation in the gas phase $\Delta H_D$

| Acid | p$K_a$ | $\Delta H_i^\ominus$ (kJ mol$^{-1}$) | $\Delta H_D$ [a] (kJ mol$^{-1}$) |
|---|---|---|---|
| $CF_3CO_2H$ | 3.45 [b] | +1.8 | 1357 |
| $CHCl_2CO_2H$ | – | +17.6 | 1376 |
| $CH_2ClCO_2H$ | 8.9 [c] | +32.2 | 1406 |
| $CH_3CO_2H$ | 12.6 [c,d] | +44.8 | 1458 |
| $C_6H_5CO_2H$ | 10.9 [c], 11.1 [d] | +38.1 | 1423 |
| 2-Nitrobenzoic | 8.18 [e] | +25.1 | |
| 3,5-Dinitrobenzoic | 7.4 [d] | +24.8 | |

[a] Ref. 16.
[b] Ref. 10.
[c] Ref. 3.
[d] Ref. 4.
[e] Ref. 5.

can be taken as the enthalpies at infinite dilution [2], $\Delta H_i^{\ominus}$, are listed in Table 2.

## DISCUSSION

We shall first examine the data for the enthalpy of solution, $\Delta H_s^{\ominus}$, of the acids, then their enthalpy of ionization $\Delta H_i^{\ominus}$, and finally we shall use some of the measured data to estimate the H-bond energy for the hydrogendiacetate ion.

### *Enthalpy of solution*

The values of the enthalpy of solution $\Delta H_s^{\ominus}$ of the acids HA in Table 1 do not show any trend which could be attributed to changes in H-bonding interactions between the acids and the basic $Me_2SO$ solvent. Since this is due in part to the different physical nature of the acids, even within the substituted acetic acids series, we took into account the enthalpy of vaporization or sublimation of the acids and their enthalpy of dimerization in the vapor phase to obtain the enthalpy of solvation $\Delta H_{gs}$ of the gaseous monomeric acids [13]. While a smoother trend of $\Delta H_{gs}$ (decreasing exothermicity from $CHCl_2CO_2H$ to $CH_3CO_2H$) was obtained, $\Delta H_{gs}$ still includes contributions other than that of H-bonding interactions. The possible evaluation of these additional contributions to the enthalpy of solvation $\Delta H_{gs}$ of the acids [14] is presently being considered.

### *Enthalpy of ionization*

The data in Table 2 show that the endothermicity of the ionization enthalpy of the substituted carboxylic acids increases from $CF_3CO_2H$ (+1.8 kJ $mol^{-1}$) to $CHCl_2CO_2H$ (+17.6 kJ $mol^{-1}$), $CH_2CClCO_2H$ (+32.2 kJ $mol^{-1}$), and $CH_3CO_2H$ (+44.8 kJ $mol^{-1}$). This is clearly unlike results for the same ionization process in water where the ionization enthalpies are less than $\pm 5$ kJ $mol^{-1}$ and show no trend. Our $\Delta H_i^{\ominus}$ value for $C_6H_5CO_2H$, +38.1 kJ $mol^{-1}$, can be compared with a +40.7 ± 5.5 kJ $mol^{-1}$ value calculated from literature data [6] using a thermochemical cycle involving $CF_3SO_3H$ as strong acid (but not $FSO_3H$) and cesium (but not lithium or potassium) dimsyl as strong base. We have previously found that a value of $\Delta H_i$ for $CH_3SO_3H$, calculated similarly using $FSO_3H$, appeared to be in error [2].

Our $\Delta H_i^{\ominus}$ values from Table 2 were plotted against the available $pK_a$ for six carboxylic acids and we obtained a fair straight line whose equation is

$$\Delta H_i^{\ominus} = (4.67 \pm 0.31)pK_a - (12.4 \pm 2.8) \qquad n = 6; \quad r = 0.991 \qquad (9)$$

This is evidence of a clear enthalpy–entropy type relationship [15] since both $\Delta H_i^\ominus$ and $pK_a$ are independently determined. While the significance of such relationships is somewhat unclear they are useful for predicting a value for $pK_a$ when $\Delta H_i^\ominus$ is known or, vice versa. A case in point here is the estimation of the $pK_a$ of $CHCl_2CO_2H$ as 6.5 from its $\Delta H_i^\ominus$ value. While the two points for the nitro-substituted benzoic acids are on or near the correlation line, more data are needed to ascertain whether eqn. (9) correlates all substituted benzoic acids.

The corresponding correlation equation

$$\Delta G_i^\ominus = (1.20 \pm 0.08)\ \Delta H_i^\ominus + (0.09 \pm 0.18) \qquad n = 6, \quad r = 0.992 \qquad (10)$$

can be compared with the equation derived for the ionization of $BH^+$ acids where B are aromatic nitrogen bases [1]

$$\Delta G_i^\ominus = (1.05 \pm 0.08)\ \Delta H_i^\ominus - (6.8 \pm 2.5) \qquad (11)$$

We note that the slopes of the correlation lines for both classes of acids AH and $BH^+$ are close but additional results for other classes of acids are needed before it can be decided whether this is a general phenomenon.

We also looked for a correlation between the acidity of the carboxylic acids in the gas phase and in $Me_2SO$ since recent values are available for $\Delta H_D$, the gas-phase enthalpy change for the deprotonation of a large number of carboxylic acids [16]. A smooth but non-linear relation is obtained when $\Delta H_D$ was plotted against $\Delta H_i^\ominus$ for $CF_3CO_2H$, $CHCl_2CO_2H$, $CH_2ClCO_2H$, $CH_3CO_2H$, and $C_6H_5CO_2H$. A linear relation would be obtained if the point for $CH_3CO_2H$ was left out but there does not seem to be any compelling reason to reject either $\Delta H_D$ or $\Delta H_i^\ominus$ for this acid.

## *H-bond energy for the hydrogendiacetate ion*

When using the hydrogendiacetate cycle to obtain $\Delta H_i$ for $CH_3CO_2H$ we found that the heat of solution of $CH_3CO_2H$ (l) in 0.2 M $NEt_4CH_3CO_2$ (reaction (5)) was $-23.1$ kJ mol$^{-1}$. By combining this value with $\Delta H_{12} = +56.1$ kJ mol$^{-1}$ [13,17] the enthalpy change for reaction (12)

$$CH_3CO_2H(l) = CH_3CO_2H(\text{monomer g}) \qquad (12)$$

we obtain $\Delta H_{13} = -74.7$ kJ mol$^{-1}$ for reaction (13)

$$CH_3CO_2H(g) + CH_3CO_2^-(s) = H(CH_3CO_2)_2^-(s) \qquad (13)$$

Now, $\Delta H_{13}$ is closely related to the H-bond energy defined for reaction (14)

$$CH_3CO_2H(g) + CH_3CO_2^-(g) = H(CH_3CO_2)_2^-(g) \qquad (14)$$

On account of ion-size alone, it is clear that the solvation enthalpy of $H(CH_3CO_2)_2^-$, $\Delta H_{gs}(HA_2^-)$, is smaller than that of $CH_3CO_2^-$, $\Delta H_{gs}(A^-)$, so that $\Delta H_{13} = -74.7$ kJ mol$^{-1}$ represents a minimum value for the H-bond energy of the hydrogendiacetate ion according to reaction (14). We then proceeded as follows to estimate $\Delta\Delta H_{gs}$, the difference between the solvation enthalpies of $CH_3CO_2^-$ and of $H(CH_3CO_2)_2^-$. First we obtained $-40$ kJ mol$^{-1}$ for $\Delta\Delta H_{gs}$, the difference between the solvation enthalpy of the pair $Cl^-$–$HCl_2^-$ in sulfolane from a gas-phase enthalpy value of $-98.3$ kJ mol$^{-1}$ for $HCl_2^-$ (reaction (14)) [18] and our $-58.2$ kJ mol$^{-1}$ value in sulfolane [7] for the reaction similar to (13). We suggest that this $-40$ kJ mol$^{-1}$ is a reasonable estimate for $\Delta\Delta H_{gs}$ for the pair $CH_3CO_2^-$–$H(CH_3CO_2)_2^-$ in $Me_2SO$. This involves both the following assumptions: first that $\Delta\Delta H_{gs}$ for both pairs $Cl^-$–$HCl_2^-$ and $CH_3CO_2^-$–$H(CH_3CO_2)_2^-$ are similar, and second that $\Delta\Delta H_{gs}$ is the same for both solvents, $Me_2SO$ and sulfolane. Both assumptions are reasonable, considering first that the enthalpies of solvation of $Cl^-$ and $CH_3CO_2^-$ in $Me_2SO$ are close [13] and second that the enthalpy of an anion–molecule reaction written as

$$X^-(s) + HR(g) = XHR^-(s) \tag{15}$$

may only vary by some 5 kJ mol$^{-1}$ from one dipolar aprotic solvent to another [19]. We finally obtained the value $-115$ kJ mol$^{-1}$ for the H-bond energy of $H(CH_3CO_2)_2^-$. This value can be compared with two values in the literature, $-125$ kJ mol$^{-1}$ [20] and $-105$ kJ mol$^{-1}$ [21], both of which required assumptions for their derivation. The $-115$ kJ mol$^{-1}$ value makes the H-bond in $H(CH_3CO_2)_2^-$ one of the strongest known [22].

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