

Estimation of the pK_a for Some Hydrocarbons and Aldehydes and Solvation Energies of the Corresponding Anions

Kim Daasbjerg

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Daasbjerg, K., 1995. Estimation of the pK_a for Some Hydrocarbons and Aldehydes and Solvation Energies of the Corresponding Anions. – Acta Chem. Scand. 49: 878–887 © Acta Chemica Scandinavica 1995.

Thermochemical cycles are used to transform previously obtained standard potentials of carbon-centred radicals $R\cdot$ into pK_a values for the corresponding weak hydrocarbon and aldehyde acids RH and into differences in solvation energies, $\Delta\Delta G_{\text{sol}}^\circ$, of the anions R^- and the radicals $R\cdot$ in *N,N*-dimethylformamide (DMF). For saturated hydrocarbons (e.g., methane and ethane) the pK_a is high and relatively constant ranging from 48 to 54. The unsaturated compounds (e.g., triphenylmethane and propene) are stronger acids having values of pK_a in the order of 29 to 41 owing to the possibility of conjugation in the corresponding anions. A similar grouping of acidities is found for aliphatic and aromatic aldehydes. Even though the uncertainty in the absolute values of pK_a is estimated to be as much as ± 5 units the consistency in the relative values is high. The values obtained in DMF are compared with corresponding results in dimethyl sulfoxide and acetonitrile and the relationship between absolute and relative acidities in these three aprotic solvents is discussed. The numerical values of $\Delta\Delta G_{\text{sol}}^\circ$ for the non-conjugated carbanions are high and relatively independent of the size of the alkyl group whereas they are smaller for the conjugated carbanions and decrease with an increase in the size of the anion. The trend in the $\Delta\Delta G_{\text{sol}}^\circ$ values is discussed.

In recent years the use of thermochemical cycles incorporating electrode potentials has achieved increased attention since it allows the extraction of thermodynamic parameters such as dissociation constants, standard potentials and bond dissociation energies, which otherwise are not easily obtainable.¹ In this paper standard potentials of carbon-centred radicals $R\cdot$ are transformed into pK_a values of the corresponding weak hydrocarbon and aldehyde acids RH and into differences in solvation energies, $\Delta\Delta G_{\text{sol}}^\circ$, of the anions R^- and the radicals $R\cdot$ in *N,N*-dimethylformamide (DMF).

Previously potentiometric, conductometric and spectrophotometric methods² have been employed for determining the equilibrium acidity in DMF of strong or relatively strong acids in the pK_a range from ca. 1 to 20. For weaker acids with pK_a ranging from 16 to 26 Vianello *et al.*³ have developed an electrochemical method. No reports have appeared focusing on the very weak acids with pK_a from 30 and upwards. Direct measurement of the equilibrium acidity is obviously not possible⁴ in this range and an estimation is only attainable indirectly. An indirect approach using thermochemical cycles and electrode potentials was first reported by Breslow *et al.*⁵ who determined the acidities of some hydrocarbons in THF–HMPA solutions. The potentials were measured by cyclic

voltammetry or second harmonic alternating current voltammetry[†] and converted into pK_a values using the known standard potential of the triphenylmethyl radical and the bond dissociation energy and pK_a of triphenylmethane as reference values.

In some cases thermodynamic parameters determined from thermochemical cycles may suffer from the use of irreversible electrode potentials. In our group we have developed an indirect electrochemical method for determining both reduction and standard potentials of radicals in DMF.⁷ It is possible to obtain these two parameters by measuring the competition between the coupling and reduction reactions that a radical can undergo with an aromatic radical anion of a known standard potential. The advantage of this method is that it provides standard potentials for highly reactive and non-conjugated alkyl radicals. Another approach has been presented by Wayner and Griller,⁸ who have measured reduction and oxidation potentials of a large number of radicals generated photolytically in small concentrations and detected by voltammetry. The potentials measured in this way may

[†] The thermodynamic significance of the potentials measured for radical–anion couples, in which the radical is involved in fast homogeneous reactions, has been questioned.⁶

be influenced by slow heterogeneous charge transfer or, less likely, fast homogeneous reactions (dimerisation, disproportionation and H-atom abstraction). However, for most conjugated systems the voltammograms are either wholly or nearly reversible and the potentials, which are measured with high precision, have direct thermodynamic significance.

The cycle that can be defined to evaluate the pK_a of an acid RH is shown in Scheme 1 and the expression for pK_a is given in eqns. (5) and (6).



Scheme 1.

$$2.303RTpK_a = \Delta G_{\text{BDE}}^{\circ} + F(E_{\text{H}^{+}/\text{H}\cdot}^{\circ} - E_{\text{R}\cdot/\text{R}^{-}}^{\circ}) \quad (5)$$

$$\Delta G_{\text{BDE}}^{\circ} \approx \Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}} + \Delta G_{\text{sol}}^{\circ}(\text{H}\cdot) - TS^{\circ}(\text{H}\cdot)_{\text{g}} \quad (6)$$

The bond dissociation Gibbs energy, $\Delta G_{\text{BDE}}^{\circ}$, is not available but can, as shown in eqn. (6), be approximated by the bond dissociation energy of RH in the gas phase, $\Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}}$, which is known for many compounds,⁹ plus two additional contributions from the Gibbs energy of solvation of $\text{H}\cdot$ in DMF, $\Delta G_{\text{sol}}^{\circ}(\text{H}\cdot)$, and the entropy of $\text{H}\cdot$ in the gas phase at 25 °C, $S^{\circ}(\text{H}\cdot)_{\text{g}}$. The latter two contributions are equal to 3.4 kcal mol⁻¹ and 27.4 cal mol⁻¹ K⁻¹ respectively.^{1,9b} The difference in the entropies of formation of RH and $\text{R}\cdot$ is normally negligible.¹⁰ The same is true for the corresponding difference in solvation energies as long as the RH bond being considered is not too polar.¹¹ For $E_{\text{H}^{+}/\text{H}\cdot}^{\circ}$ in DMF the estimated value of -2.45 V vs. NHE will be used.¹

A linear relationship between the oxidation potential of anions and the pK_a of the corresponding parent compounds has been observed experimentally in several cases within a family of substrates.^{12,13} Moreover Kern and Federlin¹³ have shown that a correlation with a dimensionless slope of 1.1 for a group of ketones could be extended to include cyclopentadiene, indene, fluorene and triphenylmethane. The slope near unity is indeed expected, as predicted by eqns. (5) and (6), as long as $\Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}}$ is reasonably constant.

In Table 1 the calculated values of pK_a for weak acids RH in DMF are shown together with previously estimated standard potentials of $\text{R}\cdot/\text{R}^{-}$ couples^{7,14,15} and bond dissociation energies.⁹ The uncertainty in pK_a is estimated to be as much as ± 5 units, which mainly can be attributed to the uncertainty on $\Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}}$ (± 2 kcal mol⁻¹) and in particular $E_{\text{R}\cdot/\text{R}^{-}}^{\circ}$ (± 150 mV) for

the non-conjugated radicals. The fact that the $E_{\text{R}\cdot/\text{R}^{-}}^{\circ}$ values for **6** and **7** are numerically higher by 200–300 mV compared with the ones obtained, with a similar high uncertainty, by comparing experimental linear sweep voltammograms of the corresponding alkyl iodides with simulated curves¹⁴ may serve as a good illustration of the difficulties and uncertainties involved in obtaining standard potentials for this kind of system. Even though the absolute pK_a values given in Table 1 should thus be used with great care, the relative values are without doubt much better determined owing to high consistency in the set of $E_{\text{R}\cdot/\text{R}^{-}}^{\circ}$. In the calculations the alternative approach suggested by Breslow *et al.*⁵ might therefore be taken into consideration using pK_a , $\Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}}$ and $E_{\text{R}\cdot/\text{R}^{-}}^{\circ}$ of diphenylmethane and triphenylmethane as reference values. The equilibrium acidities of both these compounds are known in dimethyl sulfoxide (DMSO) from direct measurements by the indicator method and as discussed later on they can be transformed into DMF values without increasing the uncertainty appreciably. These pK_a values shown in parentheses in the last column in Table 1 are higher by 1–2 units suggesting that the values calculated from eqn. (5) should be slightly increased. Unfortunately conflicting reports about the magnitude of the bond dissociation energy of triphenylmethane have appeared recently.^{9d} In the following discussion we have decided not to adjust the results given in Table 1 even though a future and more reliable determination of $\Delta H_{\text{BDE}}^{\circ}(\text{RH})_{\text{g}}$, as well as direct measurement of pK_a for diphenylmethane and triphenylmethane in DMF, may very well favour the approach proposed by Breslow *et al.*⁵

For saturated hydrocarbons (**1–10**) the pK_a values are high and relatively constant ranging from 48 to 54, while the corresponding values for the unsaturated systems (**11–21**) are smaller and in the range 29–41 owing to the possibility of charge delocalization in the corresponding anions; differences in acidities of neutral acids brought about by structural variations are usually caused by changes in the energies of the conjugated bases. Even though solvation effects will be discussed separately in the second part of this paper it may be noted at this point that the stabilization energy originating from charge delocalization is attenuated considerably in solution. A comparison of the difference in gas phase acidity, $\Delta G_{\text{acid}}^{\circ}$, of e.g., methane and triphenyl methane ($\Delta \Delta G_{\text{acid}}^{\circ} = 57$ kcal mol⁻¹)¹⁶ with the corresponding difference in solution ($2.303RT\Delta pK_a$) reveals that better solvation of the small methyl anion compared with the triphenylmethyl anion increases the stability of the former by more than 30 kcal mol⁻¹ in DMF.

The effect of α -methyl substitution in the hydrocarbons on solution acidities as well as gas phase acidities¹⁷ is negligible. For instance, the pK_a for **1**, **2**, **4** and **7** is 48, 51, 50 and 49, respectively, and for **16**, **17** and **18** it is 39, 40 and 39, respectively. The introduction of methyl groups relative to hydrogen does thus not offer any extra stabilization of the charged centre in the aliphatic anions nor does it change the solvation energies appreciably.

Table 1. Standard potentials $E_{R^{\cdot-}/R}^{\ominus}$, bond dissociation energies $\Delta H_{BDE}^{\ominus}(RH)_g$ and calculated pK_a values for some weak acids RH in DMF at 298 K. The uncertainty in pK_a is ± 5 units.

	R(H)	$-E_{R^{\cdot-}/R}^{\ominus b}$	$\Delta H_{BDE}^{\ominus}(RH)_g^e$	pK_a
1	CH ₃ (H)	0.95	105.1	48(55) ^m
2	CH ₃ CH ₂ (H)	1.40	98.2	51
3	CH ₃ CH ₂ CH ₂ (H)	1.39	97.9	50
4	(CH ₃) ₂ CH(H)	1.48	95.1	50
5	CH ₃ CH ₂ CH ₂ CH ₂ (H)	1.38	97.9 ^f	50
6	CH ₃ CH ₂ CH(H)CH ₃	1.48(1.20) ^c	95.5	50
7	(CH ₃) ₃ C(H)	1.53(1.30) ^c	93.2	49
8	Cyclo-C ₅ H ₉ (H)	1.48	94.5	49
9	Cyclo-C ₆ H ₁₁ (H)	1.44	95.5	49
10	Adamantane ^g	1.57	98.5 ^g	54
11	CH ₂ =CHCH ₂ (H)	1.15	86.3	38(44) ^m
12	CH ₂ =C(CH ₃)CH ₂ (H)	1.15	85.6	37
13	CH ₂ =CHCH(H)CH ₃	1.31	82.5	38
14	CH ₃ CH=CHCH(H)CH ₃	1.48	82.5 ^h	41
15	CH≡CCH ₂ (H)	1.01	89.4	38
16	C ₆ H ₅ CH ₂ (H)	1.16	88.0	39(43) ^m
17	C ₆ H ₅ CH(H)CH ₃	1.33	85.4	40
18	C ₆ H ₅ C(H)(CH ₃) ₂	1.33	84.4	39
19	(C ₆ H ₅) ₂ CH(H)	0.83	84	31(32.5) ^m
20	(C ₆ H ₅) ₃ C(H)	0.86 ^d	81 ⁱ	29(30.9) ^m
21	4-ClC ₆ H ₄ CH ₂ (H)	1.16	88.0 ^j	39
22	CH ₃ C(H)O	1.49	86.0	43
23	⁻ OOCCH ₂ CH ₂ C(H)O	1.51	86.0 ^k	44
24	C ₆ H ₅ CH ₂ C(H)O	1.44	86.0 ^k	42
25	C ₆ H ₅ C(H)O	0.90	86.9	34
26	4-CH ₃ OC ₆ H ₄ C(H)O	0.92	86.9 ^l	34
27	3-CH ₃ OC ₆ H ₄ C(H)O	0.91	86.9 ^l	34
28	4-ClC ₆ H ₄ C(H)O	0.78	86.9 ^l	32
29	4-CNC ₆ H ₄ C(H)O	0.78	86.9 ^l	32
30	1-Naphthalenecarbaldehyde	0.83	86.9 ^l	33

^a The H considered is at the bridgehead. ^b In V vs. NHE, Ref. 7 unless otherwise indicated. ^c From Ref. 14. ^d From Ref. 15. ^e In kcal mol⁻¹, Refs. 9(a) and 9(b) unless otherwise indicated. ^f Assumed to be the same as for **3**. ^g From Ref. 9(c). ^h Assumed to be the same as for **13**. ⁱ From Ref. 9(d). ^j Assumed to be the same as for **16**. ^k Assumed to be the same as for **22**. ^l Assumed to be the same as for **25**. ^m Calculated from eqn. (8) using the values of pK_a (DMSO) given in Ref. 21(a).

This is in direct contrast with the course in the corresponding amine and alcohol series [H₃N to (CH₃)₃N and CH₃OH to (CH₃)₃COH] in which the interaction between the methyl groups and the charged centre influences the internal stability and solvation of the ions in such a way that a reversal of basicities/acidity occurs going from gas phase to solution.¹⁸

The calculations also indicate that the acidities are strongly attenuated by saturation and steric effects when successive substitutions of hydrogen atoms by phenyl groups are made with methane. The decrease in pK_a is 9, 8 and 2 units, respectively. Adding a third phenyl group in diphenylmethyl anion thus results only in a small extra stabilization, which can be attributed mainly to the polar inductive effect of the phenyl group. Empirical charge maps have shown that the charge density on the central carbon atom of the triphenylmethyl anion turns out to be approximately the same as that present on the carbon atom of the diphenylmethyl anion.¹⁹

The pK_a values for the nine weak aldehyde acids investigated (**22–30**) can be divided into two groups, an aliphatic and an aromatic one with the latter containing

acids stronger by about 10 units. The origin of this grouping can be attributed to the effect of the aryl group which allows extensive delocalization and thereby stabilization of the negative charge in the corresponding anions.²⁰ In this context it is also of interest that the influence of substituents (including a fused benzene ring) positioned on the aryl moiety as in compounds **26–30** is small regardless of the position of the substituent.

For some of the hydrocarbons (**1**, **11**, **16**, **19** and **20**) the calculated pK_a can be compared with corresponding values in DMSO either measured by means of the indicator method²¹ or extrapolated by methods such as those described in Ref. 21(c). In general, the acidity of RH in DMF and DMSO may be interrelated taking into account the Gibbs energy of transfer ΔG_{tr}^{\ominus} for R⁻, H⁺ and RH from DMSO to DMF as shown in eqn. (7).

$$pK_a(\text{DMF}) = pK_a(\text{DMSO}) + \left(\frac{\Delta G_{tr}^{\ominus}(\text{R}^-) + \Delta G_{tr}^{\ominus}(\text{H}^+) - \Delta G_{tr}^{\ominus}(\text{RH})}{2.303RT} \right) \quad (7)$$

The difference in pK_a for a given substance in these two specific non-hydroxylic solvents is expected to be small since they are rather similar^{22,23} with respect to hydrogen-bond acceptor capabilities, polarizability ($\alpha = 7.99$ and $7.90 \times 10^{-30} \text{ m}^3$ for DMSO and DMF, respectively), dipole moment ($\mu = 3.9$ and 3.86 debye, respectively), molecular radius ($a_{\text{mol}} = 3.05$ and 3.13 \AA , respectively) and dielectric constant ($\epsilon = 46.7$ and 36.7 , respectively).[†] Indeed this expectation is borne out by the small magnitudes of the experimental known values of $\Delta G_{\text{tr}}^\circ(\text{RH})$, $\Delta G_{\text{tr}}^\circ(\text{H}^+) = 0.33 \text{ kcal mol}^{-1}$ and $\Delta G_{\text{tr}}^\circ(\text{R}^-)$ available for some relevant compounds in Ref. 25, and further confirmed by a well founded correlation shown in eqn. (8) based on a large number of solution acidities measured for benzoic acids, phenols, mono- and di-carboxylic acids, benzenesulfonamides, amides and NH-heterocycles in the pK_a range 3–26.³

$$pK_a(\text{DMF}) = 1.56 + 0.96pK_a(\text{DMSO}) \quad (r = 0.997) \quad (8)$$

In particular the high value of the correlation coefficient r indicates that the absolute acidity in one of the solvents can be calculated with a high degree of certainty from the corresponding value in the other solvent. Assuming eqn. (8) also to be valid for hydrocarbon acids, the pK_a values found in DMSO for the five compounds in question can easily be transformed into DMF values. The results of this transformation are shown in parentheses in Table 1 and as can be seen and previously noted a reasonable agreement between the two sets of values exists for the stronger acids **19** and **20**, thus supporting the validity of the thermochemical calculations. For compounds **1**, **11** and **16** the pK_a in DMSO was not directly measurable by the indicator method; the uncertainty and the deviation from the thermochemical calculations are therefore expected to be much higher in these cases. We believe that the solution acidities for the weakest acids presented in this work are more correct than the ones obtained from other methods and extrapolations.^{5b,21c}

Standard potentials of the benzylic radicals **16**, **17**, **18**, **19** and **21** have been measured in acetonitrile (CH_3CN) by modulated photolysis.⁸ The potentials are equal to those found in DMF. The Gibbs energy of transfer of R^- from CH_3CN to DMF, which can be approximated by $F[E_{\text{R}^-/\text{R}^-}^\circ(\text{CH}_3\text{CN}) - E_{\text{R}^-/\text{R}^-}^\circ(\text{DMF})]$ assuming the Gibbs energy of transfer of the radical R^\cdot to be negligible, must thus be near zero. According to eqn. (7) the difference between pK_a in the two solvents is therefore given mainly by the difference in solvent basicity as described by the Gibbs energy of transfer of the proton [$\Delta G_{\text{tr}}^\circ(\text{H}^+) \approx -15.4 \text{ kcal mol}^{-1}$]^{25a} leading to pK_a values for the benzylic compounds higher by ca. 11 units in

CH_3CN .^{*} Unfortunately the number of reliable data available for other hydrocarbon acids does not allow an extension of this correlation to a bigger pK_a range. However a survey of the literature values pertaining to numerous oxygen and nitrogen acids in DMF and CH_3CN offers the possibility of investigating whether a valuable correlation between the absolute acidities of different classes of compounds exists in the DMF– CH_3CN system as previously found in the 1-methyl-2-pyrrolidinone–DMSO²⁷ and DMF–DMSO solvent systems.³ At first glance, things look much more complicated and perhaps even more dubious in the former system. This may be illustrated by the mere fact that different degrees of homoconjugation are present in the pK_a measurements since the two solvents differ greatly in hydrogen-bond accepting capabilities.²² Depending on the polarity of the RH bond the latter circumstance should also influence the magnitude of $\Delta G_{\text{tr}}^\circ(\text{RH})$. Furthermore CH_3CN has a lower polarizability ($\alpha = 4.41 \times 10^{-30} \text{ m}^3$), a slightly smaller dipole moment ($\mu = 3.44$ debye) and a smaller molecular radius ($a_{\text{mol}} = 2.76 \text{ \AA}$) compared with DMF, whereas the two solvents have nearly the same dielectric constants ($\epsilon = 37.5$ for CH_3CN).²³ Experimental values of $\Delta G_{\text{tr}}^\circ(\text{R}^-)$ for the benzylic anions as estimated above and for a number of other anions given in Ref. 25 indicate that electrostatic effects in most cases are virtually identical in the two solvents if a small anion such as F^- is disregarded. It may be that dispersion interactions for particular cases such as the highly delocalized picrate anion²⁸ will prevail in DMF owing to the appreciably higher polarizability of this solvent, but in general the Gibbs energy of transfer of anions from CH_3CN to DMF should be near zero for delocalized anions or slightly positive ($\approx 1 \text{ kcal mol}^{-1}$) for more localized systems. The finding that DMF in general is a slightly poorer anion solvating solvent is in accordance with the magnitudes of the empirical acceptor number, AN, defined by Gutmann [$\text{AN}(\text{CH}_3\text{CN}) = 19.3$ and $\text{AN}(\text{DMF}) = 16.0$].²⁹

In Fig. 1 are reported the absolute acidities of substituted phenols, benzoic acids, monocarboxylic acids and benzenesulfonamides taken almost exclusively from the extensive compilation given in Ref. 2(a). Only compounds without internal hydrogen bonding and referenced to the same standard in each solvent have been included. Acids such as 2-substituted nitrophenols and the diprotic carboxylic acids have therefore been omitted. The data pertaining to 3,4-dichlorophenol, 2-bromophenol, 4-bromophenol, 4-chlorophenol and 3-nitrophenol have been discarded since we suspect that the values of $pK_a(\text{DMF})$, all collected from one specific research group, may be too low by about 2 units. This is supported partly by previous measurements³⁰ of $pK_a(\text{DMF})$ for

[†] The dielectric constant is correlated to a_{mol} , α and μ through the Debye equation.²⁴

* In relation to this discussion it may be noted that Scorrano *et al.*²⁶ have estimated the values of pK_a for the protonated forms of DMF, DMSO and CH_3CN in aqueous sulfuric acid to be -1.13 , -1.54 and -10 , respectively, thus illustrating the much lower basicity of acetonitrile compared with the other two solvents.

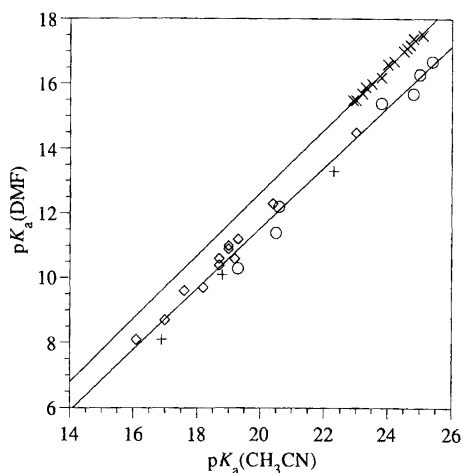


Fig. 1. Correlation between the equilibrium acidity in DMF vs. those determined in CH_3CN for substituted phenols (O), substituted benzoic acids (\diamond), monocarboxylic acids (+) and substituted benzenesulfonamides (\times).

3-nitrophenol and 4-chlorophenol giving 15.4 and 16.7, respectively, compared with the values of 13.9 and 14.3 tabulated in Ref. 2(a) and partly by the corresponding values of pK_a measured in DMSO which when transformed into DMF values by the use of eqn. (8) are indeed higher by ca. 2 units. The data given in Ref. 30 for 4-chlorophenol, 3-chlorophenol, 3-trifluoromethylphenol, 4-chlorophenol and 3-nitrophenol are included in this investigation. The compound names have been omitted in the figure for clarity and to reduce crowding but if necessary they can easily be deduced from a comparison with the data tabulated in Refs. 2(a) and 30.

As can be seen the plot is rather scattered and an immediate satisfactory relationship between $pK_a(\text{DMF})$ and $pK_a(\text{CH}_3\text{CN})$ cannot be given. However, the correlation is improved considerably if the compounds are split into two groups, the first one containing the benzenesulfonamides [eqn. (9)] and the second one the OH acids, i.e., the substituted phenols, benzoic acids and monocarboxylic acids [eqn. (10)].

$$pK_a(\text{DMF}) = -6.82 + 0.97pK_a(\text{CH}_3\text{CN}) \quad (r = 0.996) \quad (9)$$

$$pK_a(\text{DMF}) = -7.20 + 0.94pK_a(\text{CH}_3\text{CN}) \quad (r = 0.992) \quad (10)$$

The absolute difference between the pK_a values in the two solvents, ΔpK_a , is about -7.5 and -8.5 for the sulfonamides and OH acids, respectively, in the pK_a range concerned. The corresponding difference estimated above for the nonpolar hydrocarbon acids was ca. -11 . Since $\Delta G_{\text{tr}}^\circ(\text{R}^-)$ is small for the oxygen acids^{25b} as well as for the hydrocarbons the discrepancy of ca. 2.5 units between the ΔpK_a values for these two groups of acids can be attributed mainly to differences in the magnitude of $\Delta G_{\text{tr}}^\circ(\text{RH})$ for the transfer of the parent compounds between CH_3CN and DMF; the much more protophilic na-

ture of DMF compared with CH_3CN exerts a stabilizing influence on the polar OH bond in the oxygen acids whereas no such effect exists for the nonpolar C-H bond in the hydrocarbons. The slope of less than one for the OH acids may even be an indication of a correlation between pK_a and $\Delta G_{\text{tr}}^\circ(\text{RH})$, i.e., the lower the value of pK_a the more polar the OH bond and thus the higher the numerical value of $\Delta G_{\text{tr}}^\circ(\text{RH})$. If so, Hammett ρ values pertaining to the equilibrium constant for hydrogen bonding would be expected to be higher in DMF than in CH_3CN . Indeed this has been found to be the case.^{22a} For the sulfonamides hydrogen bonding should not be as important as for the oxygen acids. Still the magnitude of the term $[\Delta G_{\text{tr}}^\circ(\text{R}^-) - \Delta G_{\text{tr}}^\circ(\text{RH})]$ must be appreciable and at least of the order of 5 kcal mol^{-1} to explain the experimental results.

Intramolecular hydrogen bonding is one of the factors that cannot be easily accounted for in simple equations such as (9) and (10) and accordingly a number of 2-substituted nitrophenols as well as diprotic carboxylic acids have not been included in this investigation. The former acids have a higher pK_a in CH_3CN compared with similar acids without internal hydrogen bonding whereas the corresponding values in DMF are relatively unaffected. As an illustration of this trend it may be mentioned that $pK_a(\text{CH}_3\text{CN})$ for 2-nitrophenol and 4-nitrophenol is 22.0 and 20.6, respectively, while $pK_a(\text{DMF})$ is equal to 12.2 in both cases.^{2a} These results show that DMF, in contrast with CH_3CN , is such a strong base that it is able to break the intramolecular hydrogen bonding. Not surprisingly in this respect, DMSO behaves similarly to DMF.³¹ For a diprotic acid the conjugated (monoprotic) base is stabilized by internal hydrogen bonding in CH_3CN and the numerical value of ΔpK_a for, e.g., oxalic acid is diminished to just 5.9 units. The sterically hindered 4-nitro-2,6-di-*tert*-butylphenol has also been excluded from this investigation since its behaviour differs so much from the other phenolic acids. The presence of the bulky *tert*-butyl groups prevents any specific solvation of the alcohol group in the parent compound as well as of the oxygen site in the phenolate ion leading to negligible values of $\Delta G_{\text{tr}}^\circ(\text{RH})$ and $\Delta G_{\text{tr}}^\circ(\text{R}^-)$ and thus to a value of ΔpK_a of about -11 [$pK_a(\text{DMF}) = 8.2$ and $pK_a(\text{CH}_3\text{CN}) = 19$].³⁰

In summary it may be concluded that a general correlation between the absolute acidity of compounds in DMF and CH_3CN is not so satisfactory that accurate predictions of the pK_a value in one solvent can be obtained from the known value in the other solvent. However, reasonable correlations for the class of benzenesulfonamides [eqn. (9)] and a collection of different classes of oxygen acids such as carboxylic, phenolic and benzoic acids [eqn. (10)] are obtained if the compounds characterized by intramolecular hydrogen bonding and steric hindrance at the acidic site are omitted. For the nonpolar hydrocarbon acids $\Delta G_{\text{tr}}^\circ(\text{RH})$ and $\Delta G_{\text{tr}}^\circ(\text{R}^-)$ are negligible and ΔpK_a is given simply by $\Delta G_{\text{tr}}^\circ(\text{H}^+)/2.303RT \approx -11$, a value which is lower by ca. 3 units compared with the corresponding differences for

the sulfonamides and OH acids. As regards the values of pK_a in DMF for weak hydrocarbon and aldehyde acids estimated in this report by the use of a thermochemical cycle, the compounds can in each case be divided into two groups. For saturated hydrocarbons the pK_a is high and relatively constant ranging from 48 to 54, whereas the unsaturated compounds have a smaller pK_a in the order of 29–41 owing to the possibility of conjugation in the corresponding anions. A similar grouping of acidities is found for aliphatic and aromatic aldehydes.

In the second part of this paper the standard potentials of the radicals $R\cdot$ are transformed into differences in solvation energies, $\Delta\Delta G_{sol}^\circ$, of the anions R^- and the radicals $R\cdot$ in DMF. The opportunity given by the knowledge of $E_{R\cdot/R^-}$ to investigate solvation phenomena is of particular interest for aliphatic species since the solvation energies in these cases are not easily obtainable by other means. The formal relationship between $\Delta\Delta G_{sol}^\circ$ and $E_{R\cdot/R^-}$ as appears through the use of a thermochemical cycle has long been recognized and is given by eqn. (11).³²

$$\Delta\Delta G_{sol}^\circ = \Delta G_{sol}^\circ(R^-) - \Delta G_{sol}^\circ(R\cdot) = -\Delta G_a^\circ(R\cdot) - FE_{R\cdot/R^-} - C \quad (11)$$

The parameters $\Delta G_{sol}^\circ(R^-)$ and $\Delta G_{sol}^\circ(R\cdot)$ are the solvation energies of R^- and $R\cdot$, respectively, $\Delta G_a^\circ(R\cdot)$ is the gas phase Gibbs energy of electron attachment of $R\cdot$ and C is a constant which depends on the reference electrode. The electron attachment energies $\Delta G_a^\circ(R\cdot)$ can to a good approximation (normally to within 1 kcal mol⁻¹) be set equal to $-E_{ea}$, where E_{ea} is the electron affinity of the radicals $R\cdot$. For the constant C a number of 103.8 kcal mol⁻¹ is used, which originates from the value of the absolute potential of the normal hydrogen electrode (-4.50 V) determined as an average of five separate measurements.³³ If $\Delta\Delta G_{sol}^\circ$ is constant for a series of compounds a linear relationship between $E_{R\cdot/R^-}$ and E_{ea} with a slope of unity should exist as predicted by eqn. (11).

This relationship may be used to evaluate standard potentials from a known E_{ea} or *vice versa*, although the danger of introducing errors due to a variation in the solvation energy should always be kept in mind. The condition of constant $\Delta\Delta G_{sol}^\circ$ is normally fulfilled only for a group of large delocalized molecules where the solvation radii are close and remain reasonably constant,^{34,35} which certainly is not the case for the anions considered in this paper. Unfortunately the electron affinities are known only for some of the compounds in this report (**1–4**, **6–8**, **11**, **15**, **16**, **19**, **20** and **22**).^{16,17,36} For the benzoyl radical E_{ea} can be calculated from a thermochemical cycle incorporating the bond dissociation energy $\Delta H_{BDE}^\circ(RH)_g$, the ionization energy of the hydrogen atom (313.6 kcal mol⁻¹) and the gas phase acidity of RH, ΔH_{acid}° .¹⁶ The latter term is set equal to the calculated MNDO value of 374 kcal mol⁻¹.²⁰ Even though MNDO gas phase acidities often are quite satisfactory, especially when larger and delocalized anions are involved, the uncertainty in E_{ea} must be considered to be rather high in this case. Kleingeld *et al.*³⁷ have prepared the benzoyl anion in the gas phase but noted only a few of its reactions in order to determine its basicity. The calculated values of $\Delta\Delta G_{sol}^\circ$ are shown in Table 2 and the uncertainty is estimated to be as much as ± 6 kcal mol⁻¹. However, in the following discussion we should bear in mind that the credibility of the relative values is higher than the uncertainty of the absolute values might suggest.

Alternatively $\Delta\Delta G_{sol}^\circ$ may be derived from the solution and gas phase acidities as shown in eqn. (12) assuming $\Delta G_{sol}^\circ(RH)$ to be equal to $\Delta G_{sol}^\circ(R\cdot)$ for compounds in which the RH bonds are not too polar.

$$\Delta\Delta G_{sol}^\circ \approx \Delta G_{sol}^\circ(R^-) - \Delta G_{sol}^\circ(RH) = 2.303RTpK_a - \Delta G_{acid}^\circ - \Delta G_{sol}^\circ(H^+) \quad (12)$$

The solvation energy of the proton in DMF, $\Delta G_{sol}^\circ(H^+)$, can be calculated as -263.8 kcal mol⁻¹ us-

Table 2. Electron affinities of radicals $R\cdot$, E_{ea} , values of differences in solvation energies of the anions R^- and their corresponding radicals $R\cdot$, $\Delta\Delta G_{sol}^\circ$, molar volumes V , densities d and molecular radii a_{mol} of RH. The uncertainty in $\Delta\Delta G_{sol}^\circ$ is ± 6 kcal mol⁻¹.

	R(H)	E_{ea}^a	$-\Delta\Delta G_{sol}^\circ^e$	V^f	d^i	a_{mol}^j
1	CH ₃ (H)	1.8 ^b	80	37.8	0.424	2.5
2	CH ₃ CH ₂ (H)	-6.4	78	55.1	0.546	2.8
3	CH ₃ CH ₂ CH ₂ (H)	-1.9	74	75.9	0.581	3.1
4	(CH ₃) ₂ CH(H)	-9.5	79	75.9	0.581	3.1
6	CH ₃ CH ₂ CH(H)CH ₃	-5.8	75	96.5	0.602	3.4
7	(CH ₃) ₃ C(H)	-5.9	74	97.5	0.596	3.4
8	Cyclo-C ₅ H ₉ (H)	-7.0	77	97.8	0.717	3.4
11	CH ₂ =CHCH ₂ (H)	8.3 ^b	69	69.1	0.609	3.0
15	CH≡CCH ₂ (H)	20.6 ^b	60	59.2 ^g	0.677 ^g	2.9
16	C ₆ H ₅ CH ₂ (H)	19.9 ^b	57	117.7	0.783	3.6
22	CH ₃ C(H)O	9.8 ^c	60	56.3 ^h	0.783 ^h	2.8
25	C ₆ H ₅ C(H)O	26.5 ^d	57	122.8 ^g	0.864 ^g	3.7

^a In kcal mol⁻¹, Ref. 17 unless otherwise indicated. ^b From Ref. 16. ^c From Ref. 36. ^d Calculated from the gas phase acidity of RH, the ionization potential of H⁺ and $\Delta H_{BDE}^\circ(RH)_g$. ^e In kcal mol⁻¹. ^f In cm³ mol⁻¹, Ref. 42 unless otherwise indicated. ^g Calculated values (see the text). ^h From Ref. 9(b) at 18°C. ⁱ In g cm⁻³, Ref. 42 unless otherwise indicated. ^j In Å.

ing the estimated value of $\Delta G_{\text{sol}}^{\circ}(\text{H}^+)$ in water ($-259.5 \text{ kcal mol}^{-1}$)³³ and $\Delta G_{\text{tr}}^{\circ}(\text{H}^+)$ for the transfer of the proton between water and DMF ($-4.3 \text{ kcal mol}^{-1}$).^{25a} If $\text{p}K_{\text{a}}$ and $\Delta G_{\text{acid}}^{\circ}$ are available from direct measurements of the equilibrium acidity, evaluation of $\Delta\Delta G_{\text{sol}}^{\circ}$ from eqn. (12) compared to eqn. (11) is preferred. For a number of compounds this is indeed the case and some carbon acids relevant to this investigation are presented in Table 3 in order to improve the reliability of the whole data set. The $\text{p}K_{\text{a}}$ values are all taken from the extensive set of values available in DMSO^{21a,b} and transferred into DMF values by the use of eqn. (8) while the gas phase acidities originate from Ref. 16.

The trend in $\Delta\Delta G_{\text{sol}}^{\circ}$ is normally expected to represent the development in $\Delta G_{\text{sol}}^{\circ}(\text{R}^-)$, since the solvation of the neutral species $\text{R}\cdot$ (or RH) is negligible or at least of similar size. For the present investigation this seems to be only partly valid. Estimations of $\Delta G_{\text{sol}}^{\circ}(\text{RH})$ in water³⁸ for methane, ethane, propane, butane, 2-methylpropane, cyclopentane, propene, propyne, toluene, acetaldehyde, benzaldehyde, diphenylmethane and triphenylmethane give values of about 3.8, 3.7, 3.9, 4.0, 4.2, 3.1, 3.2, 1.4, 1.1, -1.6 , -2.1 , -0.6 and $-2.2 \text{ kcal mol}^{-1}$, respectively, the last two numbers being determined in this report by use of the bond contribution scheme presented in Ref. 38. Since the solubility of the compounds is much higher in DMF than in water, $\Delta G_{\text{sol}}^{\circ}(\text{RH})$ is expected to be smaller in this solvent. This is confirmed by some $\Delta G_{\text{sol}}^{\circ}(\text{RH})$ values available for methane, ethane, propane and butane from direct solubility measurements in DMSO, DMF and 1-methyl-2-pyrrolidinone.³⁹ The numbers concerned are all of the order of $1\text{--}2 \text{ kcal mol}^{-1}$ when transferred from unit mole fraction to unit activity standard state. From the above discussion it thus appears that the validity of the approximation $\Delta\Delta G_{\text{sol}}^{\circ} \approx \Delta G_{\text{sol}}^{\circ}(\text{R}^-)$ may be affected to some extent.

While keeping the latter finding in mind an interesting point to investigate is whether a simple correlation between $\Delta\Delta G_{\text{sol}}^{\circ}$ or $\Delta G_{\text{sol}}^{\circ}(\text{R}^-)$ and the size of the ion R^- exists for at least some of the compounds or if, in each

case, we must resort to advanced model calculations.⁴⁰ In this report the size of R^- is equated simply to the radius of the corresponding hydrocarbon RH (a_{mol}), which is determined from the molecular volume as shown in eqn. (13).

$$a_{\text{mol}} = \left(\frac{3M}{4\pi d N_{\text{A}}} \right)^{1/3} = \left(\frac{3V}{4\pi N_{\text{A}}} \right)^{1/3} \quad (13)$$

The parameter M is the molecular weight, d is the density, N_{A} is Avogadro's number and $V = M/d$ is the molar volume. Even though a spherical geometry does not seem realistic for many of the compounds shown in Tables 2 and 3 the use of eqn. (13) can still be justified considering that our purpose is solely to describe general trends and gross effects.

Unfortunately the different RH do not represent a single phase at normal temperature and pressure but are a mixture of gases, liquids and solids. The densities of RH available in the literature are therefore obtained under very different conditions and cannot easily be standardized. Consequently we have taken advantage of the fact that the density at the boiling point of liquids of similar constitution has been shown to be mainly an additive property which can be calculated from the following volume equivalents: hydrogen = $3.7 \text{ cm}^3 \text{ mol}^{-1}$, carbon = $14.8 \text{ cm}^3 \text{ mol}^{-1}$, oxygen in a carbonyl group = $12.0 \text{ cm}^3 \text{ mol}^{-1}$ and a benzene ring = $-15.0 \text{ cm}^3 \text{ mol}^{-1}$.⁴¹ The use of this procedure gives results in accordance with available literature values, the exceptions being the densities of ethane, cyclopentane, cyclopentadiene and in particular methane. For instance the calculated d of methane, ethane, propane, butane and acetaldehyde at the boiling point are 0.542, 0.581, 0.596, 0.604 and 0.781 g cm^{-3} while the experimental values are 0.424, 0.546, 0.581, 0.602 and 0.783 g cm^{-3} , respectively.^{9b,42} Moreover the radii a_{mol} are proportional to $d^{-1/3}$ which will level the effect of any error in d to a high extent. It should be emphasized that a_{mol} overesti-

Table 3. Gas phase acidities of RH , $\Delta G_{\text{acid}}^{\circ}$, $\text{p}K_{\text{a}}$ values of RH in DMF, values of differences in solvation energies of the anions R^- and their corresponding radicals $\text{R}\cdot$, $\Delta\Delta G_{\text{sol}}^{\circ}$, molar volumes V , densities d and molecular radii a_{mol} of RH . The uncertainty in $\Delta\Delta G_{\text{sol}}^{\circ}$ is $\pm 3 \text{ kcal mol}^{-1}$.

	R(H)	$\Delta G_{\text{acid}}^{\circ}$ ^a	$\text{p}K_{\text{a}}$ ^b	$-\Delta\Delta G_{\text{sol}}^{\circ}$ ^c	V ^d	d ^f	a_{mol} ^g
19	(C ₆ H ₅) ₂ CH(H)	358.3	32.5	50	206.8	0.814	4.3
20	(C ₆ H ₅) ₃ C(H)	351.7	30.9	46	295.4	0.827	4.9
31	Cyclopentadiene	347.8	18.8	58	82.4 ^e	0.802 ^e	3.2
32	Indene	344.6	20.9	52	147.8	0.786	3.9
33	Fluorene	343.9	23.3	48	199.4	0.834	4.3
34	9-Methylfluorene	343.5	23.0	48	221.6	0.813	4.4
35	9-Isopropylfluorene	343.5	23.9	47	266.0	0.783	4.7
36	9-tert-Butylfluorene	343.7	25.1	46	288.2	0.771	4.9
37	9-Neopentylfluorene	339.1	21.1	47	310.4	0.761	5.0
38	9-Phenylfluorene	335.6	18.7	46	288.0	0.841	4.9

^a In kcal mol^{-1} , Ref. 16. ^b Calculated from eqn. (8) using the values of $\text{p}K_{\text{a}}$ (DMSO) given in Refs. 21(a) and 21(b). ^c In kcal mol^{-1} . ^d In $\text{cm}^3 \text{ mol}^{-1}$, calculated values (see the text) unless otherwise indicated. ^e From Ref. 9(b) at 20°C . ^f In g cm^{-3} , calculated values (see the text) unless otherwise indicated. ^g In \AA .

mates the molecular sizes, if compared with similar radii evaluated in series of entirely solid compounds,⁴³ owing to the small magnitude of the density at the boiling point. The radii calculated in this paper should therefore not be considered to represent the correct molecular dimensions but merely as a set of sizes evaluated in a consistent manner. The molar volumes V , densities d and radii a_{mol} are given in the three last columns in Tables 2 and 3.

Fig. 2 shows a plot of the experimental solvation energies $\Delta\Delta G_{\text{sol}}^\circ$ vs. a_{mol}^{-1} . The plot is in general rather scattered but a closer look reveals that the $\Delta\Delta G_{\text{sol}}^\circ$ values can be divided into two groups. The first group contains the non-conjugated carbanions (1–4 and 6–8) with a relatively constant value of $\Delta\Delta G_{\text{sol}}^\circ$ regardless of the ion size, while the second group consists of small or conjugated carbanions (1, 11, 15, 16, 19, 20, 22, 25 and 31–38) with $\Delta\Delta G_{\text{sol}}^\circ$ correlated to a_{mol}^{-1} .

As regards the first group with the non-conjugated carbanions the average value of $\Delta\Delta G_{\text{sol}}^\circ \approx -77$ kcal mol⁻¹ is very negative. Since $\Delta G_{\text{sol}}^\circ(\text{RH})$ as previously noted is about 1–2 kcal mol⁻¹ for these specific hydrocarbons, the average value of $\Delta G_{\text{sol}}^\circ(\text{R}^-)$ is predicted to be ca. -75 kcal mol⁻¹. The solvent-exposed region for this type of anion must therefore be easily accessible and relatively independent of the alkyl chain length even to a much higher extent than found previously for some alkoxides in DMSO.⁴⁴ In fact a similar calculation of $\Delta\Delta G_{\text{sol}}^\circ$ from eqn. (12) and a_{mol} from eqn. (13) for alcohols like methanol, ethanol, 2-propanol and 2-methyl-2-propanol shows that the alkoxide ions follow nearly the same trend as the delocalized carbanions do. The different effects on solvation energies of methyl substitution in alkoxides and the non-conjugated carbanions are closely related to the charge distribution in the anions. Recent theoretical calculations show that the negative charge is, to a considerable extent, localized on one carbon in the aliphatic anions⁴⁵ whereas the greater ionic character of the C–O bond in the alkoxides spreads an appreciable amount of the negative charge to the adjacent substituents.^{18c,46}

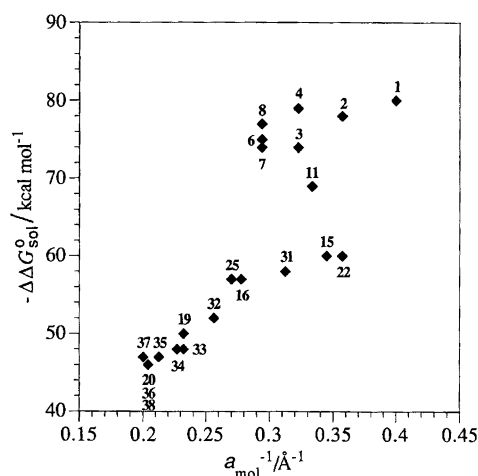


Fig. 2. Plot of $\Delta\Delta G_{\text{sol}}^\circ$ vs. a_{mol}^{-1} for some carbanions.

Spreading the charge out over a large volume element leads to a weaker interaction with the solvent and a decrease in the solvation energy.

The nearly constant solvation energy for carbanions with different alkyl chain length can actually, and even to a higher degree, be seen for the 9-substituted fluorenyl ions, grouped together with the delocalized carbanions owing to the dominant role of the fluorenyl moiety. The values of $\Delta\Delta G_{\text{sol}}^\circ$ for 33–38 are all ca. -47 kcal mol⁻¹. The fact that the bulkiness of the 9-substituent (H, methyl, isopropyl, *tert*-butyl, neopentyl, phenyl) has no influence on $\Delta\Delta G_{\text{sol}}^\circ$ indicates the absence of charge delocalization over any of the substituents, including phenyl, as well as no appreciable steric interference for solvation exerted by the substituent. This tendency, also present in DMSO, has previously been mentioned.^{21b}

For the small methyl anion and the delocalized anions in the second group a rough correlation seems to be present between $\Delta G_{\text{sol}}^\circ(\text{R}^-)$ and a_{mol}^{-1} when the contribution from $\Delta G_{\text{sol}}^\circ(\text{RH})$ is taken into account. As discussed previously the latter term probably varies by 6–10 kcal mol⁻¹ on going from methane and propene to propyne and toluene and further to substances such as cyclopentadiene, fluorene, diphenylmethane, triphenylmethane, acetaldehyde and benzaldehyde.^{38,39} At first sight the inclusion of the acetyl and propargyl anion in this second group of carbanions may seem surprising. However, theoretical calculations of the charge distributions in both the ions concerned do indicate a considerable degree of delocalization^{47,20} despite the fact that the structure of the propargyl anion is better described by an allenic-like structure.

The decrease in the numerical value of $\Delta G_{\text{sol}}^\circ(\text{R}^-)$ with increasing charge delocalization has also been observed for radical anions.^{25c,35,43a} The rough correlation between $\Delta G_{\text{sol}}^\circ(\text{R}^-)$ and a_{mol}^{-1} found for the delocalized carbanions could probably be extended, if desirable, to include solvation energies of delocalized aromatic radical anions. For instance $a_{\text{mol}}^{-1} \approx 0.23$ Å⁻¹ and the value of $\Delta\Delta G_{\text{sol}}^\circ \approx -49$ kcal mol⁻¹ measured in Ref. 25(c) for anthracene would fit well into the general picture.

The above discussion suggests that the solvation behaviour of small or delocalized anions in DMF is described rather well by the Born model. According to this model the Gibbs energy of solvation $\Delta G_{\text{sol}}^\circ(\text{R}^-)$ of a spherical ion R^- is given by eqn. (14).

$$\Delta G_{\text{sol}}^\circ(\text{R}^-)_{\text{Born}} = -\frac{N_A z^2 e^2}{8\pi\epsilon_0 a} (1 - 1/\epsilon) \quad (14)$$

The parameter z is the charge of the ion, e is the elementary charge, ϵ_0 is the permittivity of vacuum and a is the radius of the cavity formed by the ion in the solvent. The solvent is considered to be a continuum without any specific structure and the ion–solvent interaction is assumed to have no influence on the organization of the solvent molecules as a function of distance even though the in-

teraction is so much stronger in the close vicinity of the ion. Despite its simplicity the Born model has had some success in the estimation of $\Delta G_{\text{sol}}^{\ddagger}(\text{R}^-)$ values. For small anions in water a good description is actually obtained if a 'corrected' ionic radius is used as a measure of the cavity size.⁴⁸ A comparison of the slope of the best straight line through the data in the second group and the slope of 162 kcal mol⁻¹ Å in DMF as predicted by the Born equation does not really serve any purpose considering the uncertainty in the estimation of $\Delta\Delta G_{\text{sol}}^{\ddagger}$, the contribution from $\Delta G_{\text{sol}}^{\ddagger}(\text{RH})$ and $\Delta G_{\text{sol}}^{\ddagger}(\text{R}\cdot)$, the approximations in the calculations of the molecular radii from the densities at the boiling point and the overall problem in defining the radius of the cavity. Still, it does not seem likely that the Born model is applicable in DMF even on an empirical level since the contribution from $\Delta G_{\text{sol}}^{\ddagger}(\text{RH})$ or $\Delta G_{\text{sol}}^{\ddagger}(\text{R}\cdot)$ to $\Delta\Delta G_{\text{sol}}^{\ddagger}$ is expected to make the slope in a plot of $-\Delta G_{\text{sol}}^{\ddagger}(\text{R}^-)$ vs. a_{mol}^{-1} small.[†] This conclusion is further substantiated by the trend found in the solvation energies of the halide ions X^- for which the situation is less subtle and data in different solvents are available. In water as well as in DMF a linear relationship between $\Delta G_{\text{sol}}^{\ddagger}(\text{X}^-)$ and the inverted ionic radius is found but with the important difference that the magnitude of $\Delta G_{\text{sol}}^{\ddagger}(\text{X}^-)$ in the latter solvent is much less dependent on ionic size; a plot of $-\Delta G_{\text{sol}}^{\ddagger}(\text{X}^-)$ vs. (ionic radius)⁻¹ for I^- , Br^- and Cl^- using the data of Noyes⁵⁰ from aqueous media forms a straight line with a slope of 161 kcal mol⁻¹ Å ($r = 0.9999$) whereas the corresponding slope in DMF combining the data of Noyes and Marcus *et al.*^{25a} is 93 kcal mol⁻¹ Å ($r = 0.9999$). Kebarle *et al.*⁵¹ have investigated the origin of the solvation differences in water and DMF by measuring Gibbs energies for the formation of ion-molecule clusters in the gas phase. One of the main conclusions from this investigation is that the inner-shell solvation, which is dominated by ion-dipole and ion-induced dipole attractions between the ion and the molecule, decreases relatively less rapidly with increase of ion radius in DMF compared with water. This is due to the fact that the ion can approach the immediate vicinity of the water dipole whereas steric interference from the alkyl substituents in DMF prevents a similar close approach to its dipole. A further examination of the solvation past the first shell as described by the Born model shows that the Born term is more important for water than for dipolar non-hydroxylic solvents. In the latter solvents the inner-shell cluster radius is large resulting in weak Born solvation and a small decrease of this solvation with an increase of the X^- radius. The trend in $\Delta G_{\text{sol}}^{\ddagger}(\text{X}^-)$ for the sequence Cl^- , Br^- and I^- as predicted from the combined inner-shell and outer-shell studies of halide ion solvation in water and DMF is thus in accordance with the experimental trend and further-

[†] A correction of a_{mol} to more realistic molecular sizes such as 2 Å for the methyl anion⁴⁹ and 3.8 Å for the fluorenyl ion as calculated from eqn. (13) using the density 1.203 of solid fluorene would not alter this conclusion.

more in qualitative agreement with the experimental results obtained in this paper for the delocalized carbanions in DMF. Even though the spherical halide ions and the delocalized carbanions are not completely comparable in structure the solvation phenomena for the two classes of ion would be expected to be of similar type.

In summary it may be concluded that thermochemical cycles can be used to evaluate differences in solvation energies, $\Delta\Delta G_{\text{sol}}^{\ddagger}$, of carbon-centred anions R^- and the corresponding radicals $\text{R}\cdot$ or hydrocarbons RH in DMF. While the numerical values of $\Delta G_{\text{sol}}^{\ddagger}(\text{R}^-)$ for the non-conjugated carbanions are high (≈ 75 kcal mol⁻¹) and relatively independent of the size of the alkyl group, the interaction with the solvent is smaller for the delocalized carbanions. For the latter group of anions a correlation between $\Delta G_{\text{sol}}^{\ddagger}(\text{R}^-)$ and the radii a_{mol} evaluated from the molar volume exists: the bigger the radius the smaller the numerical value of $\Delta G_{\text{sol}}^{\ddagger}(\text{R}^-)$. The basic nature of solvation for delocalized carbanions in DMF seems to be of the same type as for the halide ions, i.e., dominated by inner-shell ion-dipole and ion-induced dipole attractions between the anion and the solvent molecules and is only weakly affected by an increase in the ionic radius.

Acknowledgements. Statens Naturvidenskabelige Forskningsråd is thanked for financial support.

References

- Wayner, D. D. M. and Parker, V. D. *Acc. Chem. Res.* 26 (1993) 287 and references cited therein.
- (a) Kosuke, I. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*. Chemical Data Series No. 35, Blackwell Scientific Publications, Oxford 1990; (b) Ritchie, C. D. In: Coetzee, J. F. and Ritchie, C. D., Eds., *Solute-Solvent Interactions*, Marcel Dekker, New York 1969, Chap. 4; (c) Kolthoff, I. M. and Chantooni, M. K., Jr. In: Kolthoff, I. M. and Elving, P. J., Eds., *Treatise on Analytical Chemistry*, 2nd edn., Wiley, New York 1979, Vol. 2, Chap. 19A.
- Maran, F., Celadon, D., Severin, M. G. and Vianello, E. *J. Am. Chem. Soc.* 113 (1991) 9320.
- (a) Ritchie, C. D. In: Coetzee, J. F. and Ritchie, C. D., Eds., *Solute-Solvent Interactions*, Marcel Dekker, New York 1976, Vol. 2, Chap. 12; (b) Matthews, W. S., Bares, J. E., Bartmess, J. E., Bordwell, F. G., Cornforth, F. J., Drucker, G. E., Margolin, Z., McCallum, R. J., McCollum, G. J. and Vanier, N. R. *J. Am. Chem. Soc.* 97 (1975) 7006.
- (a) Breslow, R. and Balasubramanian, K. *J. Am. Chem. Soc.* 91 (1969) 5182; (b) Breslow, R. and Goodin, R. *J. Am. Chem. Soc.* 98 (1976) 6076; (c) Breslow, R. and Grant, J. L. *J. Am. Chem. Soc.* 99 (1977) 7745; (d) Jaun, B., Schwarz, J. and Breslow, R. *J. Am. Chem. Soc.* 102 (1980) 5741.
- Andrieux, C. P., Hapiot, P., Pinson, J. and Savéant, J.-M. *J. Am. Chem. Soc.* 115 (1993) 7783.
- (a) Fuhlendorff, R., Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 43 (1989) 803; (b) Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* 44 (1990) 715; (c) Occhialini, D., Kristensen, J. S., Daasbjerg, K. and Lund, H. *Acta Chem. Scand.* 46 (1992) 474; (d) Occhialini, D., Daasbjerg, K. and Lund, H. *Acta Chem. Scand.* 47 (1993) 1100.
- (a) Wayner, D. D. M., McPhee, D. J. and Griller, D. *J. Am. Chem. Soc.* 110 (1988) 132; (b) Sim, B. A., Griller, D. and

- Wayner, D. D. M. *J. Am. Chem. Soc.* 111 (1989) 754;
 (c) Milne, P. H., Wayner, D. D. M., DeCosta, D. P. and Pincok, J. A. *Can. J. Chem.* 70 (1992) 121.
9. (a) McMillen, D. F. and Golden, D. M. *Ann. Rev. Phys. Chem.* 33 (1982) 493; (b) *CRC Handbook of Chemistry and Physics*, Lide, D. R., Ed., CRC Press, Boca Raton, FL 1991; (c) Kruppa, G. H. and Beauchamp, J. L. *J. Am. Chem. Soc.* 108 (1986) 2162; (d) Bordwell, F. G., Cheng, J.-P. and Harrelson, J. A., Jr. *J. Am. Chem. Soc.* 110 (1988) 1229.
 10. Benson, S. W. *Thermochemical Kinetics*, 2nd edn., Wiley, New York 1976.
 11. Pearson, R. G. *J. Am. Chem. Soc.* 108 (1986) 6109.
 12. (a) Bordwell, F. G. and Bausch, M. J. *J. Am. Chem. Soc.* 108 (1986) 1979; (b) Bordwell, F. G., Cheng, J.-P., Bausch, M. J. and Bares, J. E. *J. Phys. Org. Chem.* 1 (1988) 209; (c) Bordwell, F. G., Harrelson, J. A., Jr. and Satish, A. V. *J. Org. Chem.* 54 (1989) 3101.
 13. (a) Kern, J. M. and Federlin, P. *Tetrahedron* 34 (1978) 661; (b) Kern, J. M., Sauer, J. D. and Federlin, P. *Tetrahedron* 38 (1982) 3023.
 14. Andrieux, C. P., Gallardo, I. and Savéant, J.-M. *J. Am. Chem. Soc.* 111 (1989) 1620.
 15. Capobianco, G., Farnia, G., Severin, M. G. and Vianello, E. *J. Electroanal. Chem.* 165 (1984) 251.
 16. Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D. and Mallard, W. G. *J. Phys. Chem. Ref. Data* 17 (1988) Suppl. 1.
 17. DePuy, C. H., Gronert, S., Barlow, S. E., Bierbaum, V. M. and Damrauer, R. *J. Am. Chem. Soc.* 111 (1989) 1968.
 18. (a) Aue, D. H., Webb, H. M. and Bowers, M. T. *J. Am. Chem. Soc.* 98 (1976) 318; (b) Tuñón, I., Silla, E. and Tomasi, J. *J. Phys. Chem.* 96 (1992) 9043; (c) Tuñón, I., Silla, E. and Pascual-Ahuir, J.-L. *J. Am. Chem. Soc.* 115 (1993) 2226.
 19. Bradamante, S. and Pagani, G. A. *J. Org. Chem.* 49 (1984) 2863.
 20. Chandrasekhar, J., Andrade, J. G. and Schleyer, P. v. R. *J. Am. Chem. Soc.* 103 (1981) 5612.
 21. (a) Bordwell, F. G. *Acc. Chem. Res.* 21 (1988) 456; (b) Taft, R. W. and Bordwell, F. G. *Acc. Chem. Res.* 21 (1988) 463; (c) Bordwell, F. G. and Algrim, D. J. *J. Am. Chem. Soc.* 110 (1988) 2964.
 22. (a) Nielsen, M. F. *Acta Chem. Scand.* 46 (1992) 533; (b) Nielsen, M. F. and Hammerich, O. *Acta Chem. Scand.* 46 (1992) 883.
 23. Marcus, Y. *Ion Solvation*, Wiley, Chichester 1985, Chap. 6.
 24. For instance, see: Atkins, P. W. *Physical Chemistry*, Oxford University Press, Oxford 1990, 4th edn., p. 650.
 25. (a) Marcus, Y., Kamlet, M. J. and Taft, R. W. *J. Phys. Chem.* 92 (1988) 3613; (b) Chantooni, M. K., Jr. and Kolthoff, I. M. *J. Phys. Chem.* 77 (1973) 527; (c) Shalev, H. and Evans, D. H. *J. Am. Chem. Soc.* 111 (1989) 2667.
 26. Bagnò, A. and Scorrano, G. *J. Am. Chem. Soc.* 110 (1988) 4577.
 27. Bordwell, F. G., Branca, J. C., Hughes, D. L. and Olmstead, W. N. *J. Org. Chem.* 45 (1980) 3305.
 28. Grunwald, E. and Price, E. *J. Am. Chem. Soc.* 86 (1964) 4517.
 29. Gutmann, V. *Electrochim. Acta* 21 (1976) 661.
 30. Chantooni, M. K., Jr. and Kolthoff, I. M. *J. Phys. Chem.* 80 (1976) 1306.
 31. Kolthoff, I. M., Chantooni, M. K., Jr. and Bhowmik, S. *J. Am. Chem. Soc.* 90 (1968) 23.
 32. (a) Matsen, F. A. *J. Chem. Phys.* 24 (1956) 602; (b) Peover, M. E. *Trans. Faraday Soc.* 58 (1962) 1656.
 33. Lim, C., Bashford, D. and Karplus, M. *J. Phys. Chem.* 95 (1991) 5610.
 34. Dewar, M. J. S., Hashmall, J. A. and Trinajstić, N. *J. Am. Chem. Soc.* 92 (1970) 5555.
 35. (a) Chowdhury, S., Grimsrud, E. P. and Kebarle, P. *J. Phys. Chem.* 91 (1987) 2551; (b) Heinis, T., Chowdhury, S., Scott, S. L. and Kebarle, P. *J. Am. Chem. Soc.* 110 (1988) 400; (c) Crocker, L., Wang, T. and Kebarle, P. *J. Am. Chem. Soc.* 115 (1993) 7818.
 36. Nimlos, M. R., Soderquist, J. A. and Ellison, G. B. *J. Am. Chem. Soc.* 111 (1989) 7675.
 37. Kleingeld, J. C. and Nibbering, N. M. M. *Tetrahedron* 40 (1984) 2789.
 38. Hine, J. and Mookerjee, P. K. *J. Org. Chem.* 40 (1975) 292.
 39. *IUPAC Solubility Data Series*, Pergamon Press, Oxford (a) *Methane*, Clever, H. L. and Young, C. L., Eds., Vol. 27/28, 1987; (b) *Ethane*, Hayduk, W., Ed., Vol. 9, 1982; (c) *Propane, Butane and 2-Methylpropane*, Hayduk, W., Ed., Vol. 24, 1986.
 40. (a) Gilson, M. K. and Honig, B. *Proteins* 4 (1987) 7; (b) Jorgensen, W. L. and Gao, J. *J. Am. Chem. Soc.* 110 (1988) 4212; (c) Jean-Charles, A., Nicholls, A., Sharp, K., Honig, B., Tempczyk, A., Hendrickson, T. F. and Still, W. C. *J. Am. Chem. Soc.* 113 (1991) 1454.
 41. Glasstone, S. and Lewis, D. *Elements of Physical Chemistry*, 2nd edn., Macmillan, London 1968, p. 265.
 42. (a) *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh 1953; (b) *Physical Constants of Hydrocarbons*, ASTM Technical Publication No. 109A; American Society for Testing and Materials, Philadelphia 1963.
 43. (a) Peover, M. E. *Electrochim. Acta* 13 (1968) 1083; (b) Kojima, H. and Bard, A. J. *J. Am. Chem. Soc.* 97 (1975) 6317.
 44. (a) Arnett, E. M., Small, L. E., McIver, R. T., Jr. and Miller, J. S. *J. Am. Chem. Soc.* 96 (1974) 5638; (b) Arnett, E. M., Johnston, D. E. and Small, L. E. *J. Am. Chem. Soc.* 97 (1975) 5598.
 45. (a) Wiberg, K. B., Breneman, C. M. and LePage, T. J. *J. Am. Chem. Soc.* 112 (1990) 61; (b) Moffat, J. B. *J. Am. Chem. Soc.* 104 (1982) 3949.
 46. (a) Wiberg, K. B. *J. Am. Chem. Soc.* 112 (1990) 3379.
 47. Wilmshurst, J. K. and Dykstra, C. E. *J. Am. Chem. Soc.* 102 (1980) 4668.
 48. (a) Latimer, W. M., Pitzer, K. S. and Slansky, C. M. *J. Chem. Phys.* 7 (1939) 108; (b) Rashin, A. A. and Honig, B. *J. Phys. Chem.* 89 (1985) 5588.
 49. Pauling, L. *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, New York 1960, p. 261.
 50. (a) Noyes, R. M. *J. Am. Chem. Soc.* 84 (1962) 513; (b) *ibid.* 86 (1964) 971.
 51. (a) Davidson, W. R. and Kebarle, P. *J. Am. Chem. Soc.* 98 (1976) 6125; (b) Magnera, T. F., Caldwell, G., Sunner, J., Ikuta, S. and Kebarle, P. *J. Am. Chem. Soc.* 106 (1984) 6140; (c) Kebarle, P., Caldwell, G., Magnera, T. and Sunner, J. *Pure Appl. Chem.* 57 (1985) 339.

Received February 3, 1995.