Ions-gas phase and solution-dipolar aprotic solvents

P. Kebarle, G. Caldwell, T. Magnera, J. Sunner

Department of Chemistry, University of Alberta, Edmonton,
Canada T6G 2G2

Abstract – Gas phase ion-molecule equilibria measure-
ments provide thermochemical data with which the
enthalpies and free energies of formation of ions in
the gas phase can be obtained. These combined with
the corresponding energies in solution provide ion
solvation energies. The interpretation of solvation
energies is aided by thermochemical results from gas
phase ion-solvent molecule equilibria: $X^- + nL =$
X^-L_n. This approach is applied to an elucidation of
the factors causing faster kinetic rates of re-
actions: $X^- + B \rightarrow$ products, in dipolar aprotic
solvents and the smaller decrease of negative ion
solvation in dipolar aprotic solvents with increase
of ion size and charge delocalization in the ion.

I. INTRODUCTION

When one deals with ions in many different solvent environments it becomes
particularly sensible to separate the intrinsic, molecular properties of the
ion from the properties due to the interaction of the ion with the solvent.
For example, the energy changes of a simple acid-base proton transfer re-
action like 1 are strongly solvent dependent. While aqueous solution was and

$$AH + B^- = A^- + BH \tag{1}$$

is often used as the normative solvent relative to which the energy changes
in other solvents were compared, there are many advantages to comparison not
with water but with the dilute gas phase. One obvious advantage is that one
can compare the complex situation in solution with the simple state in the
gas phase, while before one was comparing one complex and poorly understood
situation with another. Another advantage is the possibility to determine
the acidity of all acids in the gas phase, from the weakest like CH_4 to the
strongest while in solution, due to the leveling effect of the solvent or
solubility problems, only a given range of acids can be measured in a given
solvent.

Until not too long ago, the use of the gas phase as a comparison state was
not a practicable approach because there was great paucity of information on
the energy changes of reactions like (1) in the gas phase. The development
of ion-molecule equilibrium measurements in the gas phase, Kebarle (1),
Bowers (2), has completely changed the situation of gas phase energetics.
Abundant data are now available and the store continues to increase, Kebarle
(3), Aue (4), McIver (4), Lias (5). While it has proven possible to measure
ion molecule equilibria involving a large variety of reaction types and
leading to the ion thermochemistry of many different classes of ions, for the
present purposes we need consider only two types. One is the proton transfer
reaction (1) already mentioned. Measurement of equilibria (1) leads via eq.
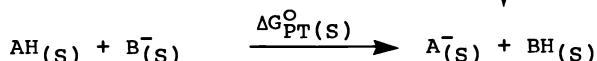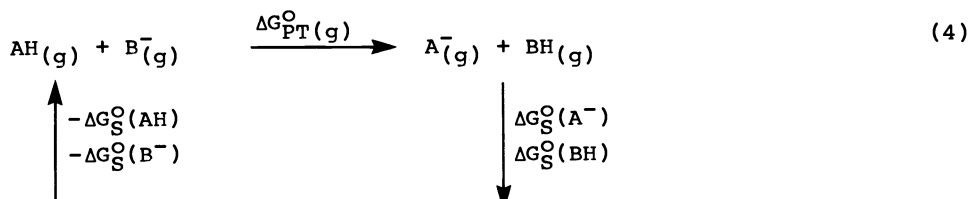2 to the free energy change, while determinations of the equilibrium

$$K_1 = \frac{[A^-][BH]}{[B^-][AH]} \qquad \Delta G_1^O = -RTlnK_1 \tag{2}$$

constants at different temperatures lead via a van't Hoff plot to the ΔH_1^O

change. One can then directly compare relative acidities in the gas phase with relative acidities in a given solvent, S, where $\Delta G^O_{1(S)}$ can be evaluated from (3) the acidity constants and eq. 3.

$$\Delta G^O_{1(S)} = 2.3 \; R(pK_{BH}-pK_{AH}) \tag{3}$$

It is also possible to obtain the (relative) solvation energies ΔG^O_S of the anions A^- and B^- with use of the Born cycle 4 and resulting eq. 5. The

$$AH_{(g)} + B^-_{(g)} \xrightarrow{\Delta G^O_{PT(g)}} A^-_{(g)} + BH_{(g)} \tag{4}$$

$-\Delta G^O_S(AH)$
$-\Delta G^O_S(B^-)$

$\Delta G^O_S(A^-)$
$\Delta G^O_S(BH)$

$$AH_{(S)} + B^-_{(S)} \xrightarrow{\Delta G^O_{PT(S)}} A^-_{(S)} + BH_{(S)}$$

$$\Delta G^O_S(A^-) - \Delta G^O_S(B^-) = \Delta G^O_{PT(S)} - \Delta G^O_{PT(g)} + \Delta G^O_S(AH) - \Delta G^O_S(BH) \tag{5}$$

solvation energies of the ions (ΔG^O_S or ΔH^O_S) are in the fundamental units for the thermochemistry of ions in solution once one accepts the gas phase as the reference environment.

Even when the solvation energies of the ions are available, understanding of the effect of the solvent on a molecular level may be lacking. Very useful information towards this aspect is provided by the energy changes for sequential solvent molecule additions to the ion. These are obtained from the second type of equilibrium, which is shown in eq. 6 for the negative ion X^- and the solvent (ligand) molecule L. The sequential equilbria (6) can be

$$X^-L_{n-1} + L = X^-L_n \qquad (n-1,n) \tag{6}$$

$$X^- + nL = X^-L_n \qquad (o,n) \tag{7}$$

experimentally measured, from the resulting $\Delta G^O_{n-1,n}$ (or $\Delta H^O_{n-1,n}$) one can also evaluate $\Delta G^O_{o,n}$ (or $\Delta H^O_{o,n}$) defined in eq. 7. Measurements for n up to 4-9 are generally possible, such that information on the strong initial interactions, for the inner shell and somewhat beyond it, are obtained. For reviews of this approach see Kebarle (3), (6). The results in Fig. 1, from Dzidic (7), demonstrate that the information is
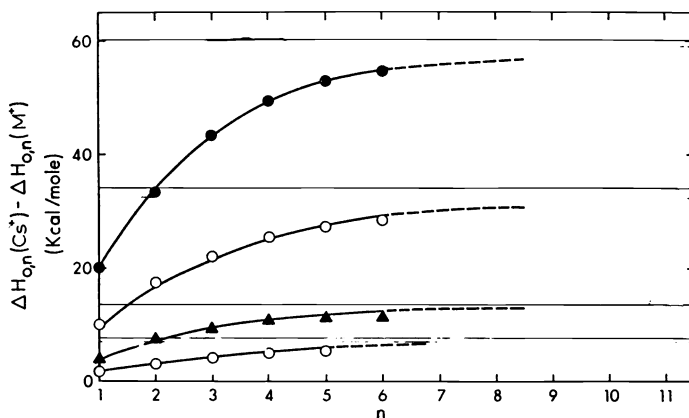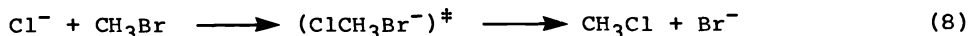

Fig. 1. Gas phase hydration enthalpies, $\Delta H^O_{o,n}$ for $M^+ + nH_2O = M^+(H_2O)_n$ where M^+ = ● Li^+, ○ Na^+, ▲ K^+, ○ Rb^+. Hydration differences $\delta\Delta H_{o,n}$ approach hydration differences in liquid H_2O (horizontal lines) at high n.

relevant to the situation in solution. The $\Delta H^O_{o,n}$ (Cs$^+$) $-$ $\Delta H^O_{o,n}$ (M$^+$) are
plotted versus the corresponding hydration enthalpy difference in the liquid
solvent. The gas phase data approach already, within the experimentally
accessible n, the hydration energy in solution. Thus, at least for these
simple spherical ions the magnitudes of relative solvation energies in solu-
tion are reflected to a large extent by the initial, strong ion solvent
molecule interactions measured in the gas phase.

II.   SOLVATION OF NEGATIVE IONS IN DIPOLAR APROTIC SOLVENTS

a. Effects of solvation on rates of reactions of the type A$^-$ + B →
products. S$_N$2 reactions.

We shall consider specifically the S$_N$2 reaction 8 but much of the discussion
will be equally applicable to the general reaction 9.

$$Cl^- + CH_3Br \longrightarrow (ClCH_3Br^-)^{\ddagger} \longrightarrow CH_3Cl + Br^- \qquad (8)$$

$$A^- + B \longrightarrow (AB^-)^{\ddagger} \longrightarrow \text{products} \qquad (9)$$

The reaction coordinate of (8) in the gas phase is shown in Fig. 2. It is
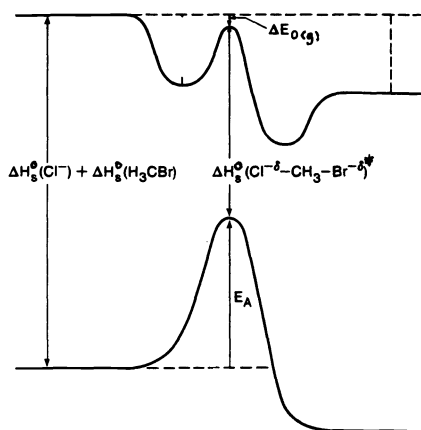
Fig. 2. Reaction coordinate for reaction:
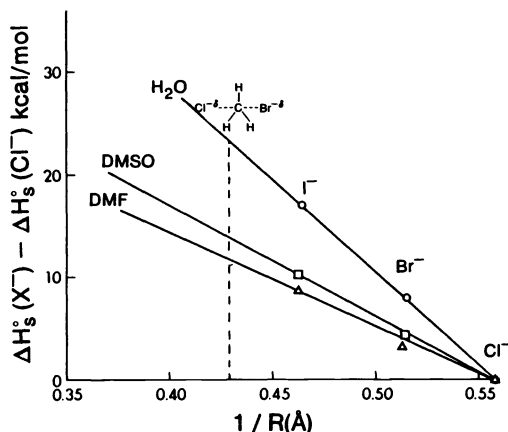Cl$^-$ + CH$_3$Br = ClCH$_3$ + Br$^-$ in gas phase and
solution.

Fig. 3. Solvation enthalpies of ions X$^-$ in
liquid solvents, relative to Cl$^-$. Pauling
radii used for Cl$^-$, Br$^-$, I$^-$.

based on measurements of the reaction kinetics of 8 in the gas phase, Brauman
(8), Caldwell (9). It is important to note that the energy of the transition
state is less than that of the reactants. The energy barrier for the forma-
tion of the transition state is smaller than the energy lowering due the
attraction between the ion with the dipole and polarizability of the mole-
cule. The Born type cycle shown in Fig. 2 leads to eq. 10 for the E_A i.e.

$$E_A = \Delta E_{o(g)} + \Delta H^O_S(Cl^{-\delta}-CH_3-Br^{-\delta})^{\ddagger} - \Delta H^O_S(Cl^-) - \Delta H^O_S(CH_3Br) \qquad (10)$$

the activation energy in solution.   Since $\Delta E_{o(g)}$ and $\Delta H^O_S(CH_3Br)$ are rela-
tively small, E_A is dominated by the difference of the solvation energy of
the transition state and the reactant Cl$^-$ ion. This difference is positive
because the transition state, being a larger ion is less exothermically
solvated than the reactant ion.

S$_N$2 reactions like 8 are known to proceed much faster in dipolar aprotic sol-
vents than in protic solvents. The rate differences may be as large as 10^7
and are due to a smaller E_A in the aprotic solvents. Much effort has gone
into the interpretation of the reasons for these differences and many useful
insights have been obtained, Parker (10); however, we feel the present dis-
cussion, from Magnera (11), based on eq. 10 and data to be discussed pro-
vides an improved picture.

The solvation energies in the ligand solvents for the ions X$^-$ (I$^-$, Br$^-$)
relative to Cl$^-$ are shown in Fig. 3. For references to these literature data

see Magnera (11). These results demonstrate that the solvation energies of X^- in protic and aprotic solvents decrease with increase of the ion radius, however, the decrease is considerably smaller for the aprotic solvents. An accurate "radius" for the transition state can not be assigned. The radius chosen as indicated in Fig. 3 is arbitrary but falls within a reasonable range. The solvation energies obtained from Fig. 3 and this choice for the transition state, when substituted in eq. 10 lead to the activation energies for H_2O and DMF shown in Table 1. Both values are in good agreement with the experimental E_A.

TABLE 1. Activation Energy E_A in solution for reaction
$$Cl^- + CH_3Br = ClCH_3 + Br^{-a}$$

Solvent	E_A predicted[b]	E_A experimental[c]
H_2O	26	25
DMF	17	18

a. Units kcal/mol. b. eq. 10. c. Parker (10).

Considering the general reaction: $A^- + B \rightarrow (AB^-)^{\ddagger}$, since the transition state will always be larger than the reactant ion A^-, it follows that the lesser decrease of solvation with increasing ion size in dipolar aprotic solvents will generally provide very much higher rates in these solvents - a very important advantage in synthetic work.

b. Solvation and ion size in protic and aprotic solvents

We now will address the question: what are the causes for the smaller decrease of solvation exothermicity with increase of ion radius (ion size) in aprotic solvents? (See Fig. 3). Results from the gas phase clustering equilibria of X^- (and M^+) with aprotic and protic solvents provide direct insights. The enthalpy changes $\Delta H^O_{n-1,n}$ for Cl^-, Br^-, I^- and K^+ and DMSO are shown in Fig. 4. Much stronger interactions particularly at low solvent number n are observed for the positive ion. Similarly stronger interactions for the positive ion have been observed also for acetonitrile, Davidson (12) and acetone, Magnera (11). A plot of $\Delta G^O_{o,n}(Cl^-) - \Delta G^O_{o,n}(K^+)$ for acetonitrile versus n is shown in Fig. 5. The $\delta\Delta G^O_{o,n}$ is seen to approach at high n the corresponding solvation energy difference in the liquid solvent. Unfortunately, the latter value is not accurately known, Davidson (12). The enthalpy changes for K^+ and X^- associating with protic and aprotic solvent molecules are shown in Table 2. For the protic water the exothermicity for
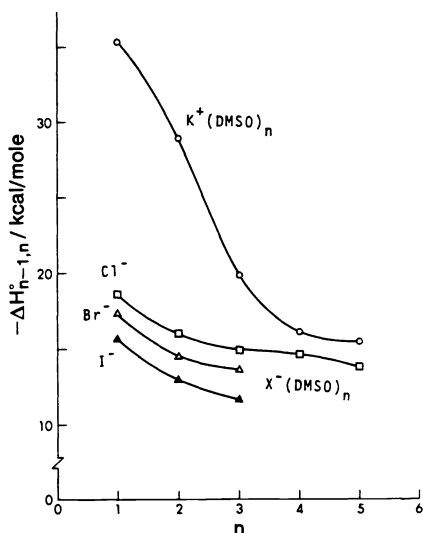

Fig. 4. Enthalpies $\Delta H^O_{n-1,n}$ for gas phase reactions: $X^-(DMSO)_{n-1} + DMSO = X^-(DMSO)_n$, and same reactions for K^+.
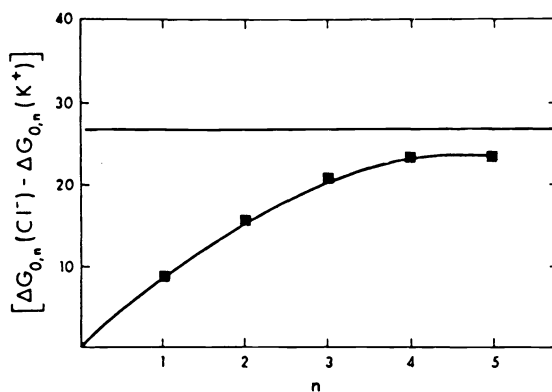

Fig. 5. Plot of $\Delta G^O_{o,n}(Cl^-) - \Delta G^O_{o,n}(K^+)$ for acetonitrile versus n. Gas phase result approaches result in solution (horizontal line) already at low n.

TABLE 2. Energy changes for reactions: $K^+ + nL = K^+L_n$ and $X^- + nL = X^-L_n$ (kcal/mol)[a]

L	μ^d	$-\Delta H^O_{o,1}$			$\delta\Delta H^O_{o,1}$	$-\Delta H^O_{o,4}$		$\delta\Delta H^O_{o,4}$
		K^+	Cl^-	I^-	(I^-,Cl^-)	Cl^-	I^-	(I^-,Cl^-)
H_2O	1.8	16.9	14.6[c]	10.3	4.3	49.0	~38.5	~11
MeCN	3.9	24.4	13.4	11.9	1.5	42.4	~39.7	~ 2.7
Me_2Co^b	2.9	26.0	14.0	12.0	2.0	-	-	-
Me_2So^b	4.1	34.5	18.6	15.7	3.1	64.1	~51.5	~12.6

a. Kebarle (3); b. Magnera (11); c. Caldwell, Kebarle recent unpublished result; d. dipole moment in Debye units.

K^+ is only slightly larger than that for Cl^-, while aprotic solvents have exothermicities with K^+ that are nearly twice as large as for Cl^-. The reasons for this difference are easily understood. The different orientation of the dipolar aprotic molecules towards the positive and negative ion (see Fig. 6) place the major site of the molecular dipole and polarizability, i.e. the S=O in DMSO and C≡N for acetonitrile, much further away from the negative ion. The structures in Fig. 6 are based on molecular orbital calculations with 4-31G basis set and an improved basis set for K^+. The data for DMSO are from Magnera (11) while those for acetonitrile are from Hirao (13,14). The calculated binding energies are in good agreement with the experimental $\Delta H^O_{o,1}$ values. The Cl^- lines up with the dipole of the functional group (S=O or C≡N). The approach of the negative ion to the functional group is hindered due to the presence of methyl for both DMSO and acetonitrile, but since DMSO is pyramidal the two methyl groups keep partially out of the way and the approach of Cl^- is not completely barred. This is not so for the linear acetonitrile where the methyl group is completely in the way of the negative ion. The same strong steric blockage should also occur for acetone. The net atomic charges obtained from Mulliken population analysis also are given in Fig. 6. These show that only 0.002 electrons are transferred to K^+ on formation of the DMSO comples. The electron transfer on formation of the Cl^- DMSO complex (0.060 electrons) is somewhat larger but still quite small. The bonding in both cases is largely electrostatic.

Considering the negative ions X^- in protic and dipolar aprotic solvents, one may conclude from the data in Table 2 and structures in Fig. 6 that because the dipole and polarizability of the aprotic molecule is located some distance away from the ion, the strength of interaction will decrease relatively less rapidly with increase of ion radius, than would be the case for protic solvents like water whose dipole can approach the immediate vicinity of the ion. The $\Delta H^O_{o,4}$ for attachment of four solvent molecules to Cl^- and I^- are given in Table 2 for H_2O, CH_3CN and DMSO. The $\delta\Delta H^O_{o,1} = \Delta H^O_{o,1}$ $(I^-) - \Delta H_{o,1}$ (Cl^-) and the corresponding $\delta\Delta H^O_{o,4}$ also are shown in Table 2. Acetonitrile and acetone when compared to water show the expected trend i.e. the $\delta\Delta H^O_{o,1}$ values for these two aprotic solvents are considerably smaller than that for
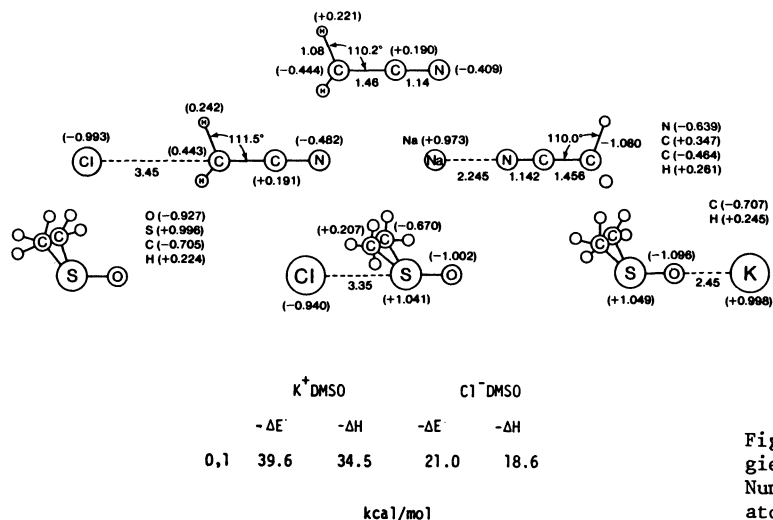

	K^+DMSO		Cl^-DMSO	
	$-\Delta E$	$-\Delta H$	$-\Delta E$	$-\Delta H$
0,1	39.6	34.5	21.0	18.6

kcal/mol

Fig. 6. Structures and energies ΔE from 4-31G calculations. Numbers in brackets are net atomic charges.

water. For example, $\delta\Delta H^O_{O,4}$ (H_2O) ≈ 11 kcal/mol while that for MeCN is only ~3 kcal/mol. Thus, for these two solvents, the lesser decrease of solvation in the liquid solvent with increase of X^- radius is at least partially due to the large distance between the ion and the dipole of the solvent molecules in the first shell. For DMSO the decrease of solvation ($\delta\Delta H_{O,4}$) between Cl^- and I^- is not smaller than that in H_2O but approximately the same. This special behaviour of DMSO should be attributed to the aforementioned ability of the negative ion to approach the S=O dipole, due to the pyramidal structure of Me_2SO, and the very high dipole moment of this solvent molecule. These result in strong binding to X^-. The binding energies X^- to DMSO are appreciably higher than those for X^-H_2O, thus Cl^-H_2O, 14.6 kcal/mol while Cl^-DMSO 18.6 kcal/mol (Table 2). Thus, the lesser sensitivity of DMSO solvation on X^- radius (Fig. 3) can not be based on first shell solvation.

An examination, Magnera (11), of the solvation past the first shell, largely on basis of the Born eq. 11 where r is the radius of the inner shell cluster,

$$\Delta G^O_{Born} = -\frac{165.2}{r(Å)}\left(1 - \frac{1}{D}\right)\frac{kcal}{mol} \tag{11}$$

D the dielectric constant of the solvent, shows that for small protic molecules like water solvation past the first shell makes a substantial contribution to the total solvation. Furthermore, the solvation past the first shell decreases significantly with increase of the radius of the core ion X^-. Dipolar aprotic molecules like acetonitrile, acetone, DMSO are bulky and lead to a large inner shell cluster radius, weak solvation past the inner shell and only small decreases of this solvation with increase of X^- radius.

In summary, dipolar aprotic solvents like acetonitrile, acetone and probably also DMF and DMA and others, lead to X^- solvation which is insensitive to ion radius because effective steric interference of the alkyl groups keeps the dipole of the functional group of inner shell molecules at a large distance from X^-. In addition to this the solvation past the inner shell in dipolar aprotic solvents is weak and the decreases resulting from ion radius increase small. For DMSO, this second effect seems to be the major one.

Results in Figs. 4, 5, 6 demonstrated that positive ions are strongly solvated by dipolar aprotic solvents due to particularly strong interactions of the ion with the solvent molecules in the first shell. The $\Delta H^O_{O,1}$ and $\Delta G^O_{O,1}$ results in Table 3, from Sunner (15), expand the data to a larger number of solvents. The binding energies of K^+ with DMSO, DMA and DMF are seen to be even bigger than those with the bidentate ligands $MeOCH_2CH_2OMe$ (Glyme) and 1,2 diaminoethane. The strong solvation of the positive ions in dipolar aprotic solvents is particularly useful in synthetic work (reactions 8 and 9). It promotes the solubility of the MX salt and by complexing with M^+ prevents the formation of ion pairs M^+X^-, thus keeping the reactivity of X^- high.

TABLE 3. Energy changes for reactions: $K^+ + L = K^+L$ in the gas phase.[a]

L	$-\Delta H^O$ (kcal/mol)	$-\Delta G^{O\,c}$ (kcal/mol)	μ^b	L	$-\Delta H^O$ (kcal/mol)	$-\Delta G^O$ (kcal/mol)	μ^b
DMSO	35	25	3.9	Me_2CO	26	19	2.9
DMA	31	24	3.8	MeCN	24	18	3.9
DMF	31	23	3.9	Me_2O	21	13	1.3
$(MeOCH_2)_2$	31	23		NH_3	18	12	1.5
$(NH_2CH_2)_2$	26	19		H_2O	17	11	1.8

a. Sunner (15); b. dipole moment in Debye; c. standard state 1Atm., 298K.

c. Acidities and delocalized anions in dipolar aprotic solvents.
A comparison between the acidities for substituted phenols in the gas phase, McMahon (16), Taft (17), H_2O, and DMSO, Bordwell (18) is shown in Fig. 7. The plots show that an approximately linear relationship exists between the acidities in the gas phase and the aqueous or DMSO solution. This can be
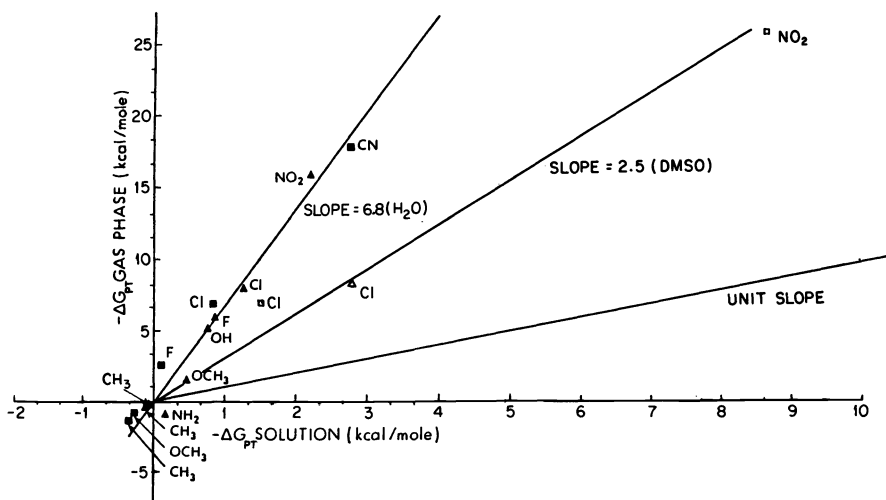
Fig. 7. Acidities of substituted phenols in the gas phase, in H_2O and in DMSO solution. ΔG^O_{PT} for proton transfer reaction: $A^-_O + AH = A_OH + A^-$, where A_OH is phenol and AH is a substituted phenol ■ para, ▲ meta substituent.

expressed by eq. 12 for the proton transfer reaction 13 where A_OH is phenol

$$\Delta G^O_{PT}(g) \approx \rho\ \Delta G^O_{PT}(s) \tag{12}$$

$$A^-_O + AH = A_OH + A^- \qquad (PT) \tag{13}$$

and AH is a substituted phenol. The value of ρ is approximately 7 for H_2O and 2.5 for DMSO, i.e. the substituent effect is attenuated by a factor of 7 in H_2O and 2.5 in DMSO. It is easy to show, see Born cycle (4-5), that eq. 12 leads to the approximate relationship 14, if the small solvation energy

$$\delta\Delta G^O_S(A^-) = \Delta G^O_S(A^-) - \Delta G^O_S(A^-_O) \approx -c\ \Delta G^O_{PT}(g) \tag{14}$$

$$c = (1 - \frac{1}{\rho}) \approx 0.86\ (H_2O)$$

$$\approx 0.6\ (DMSO)$$

difference $\delta\Delta G_S(AH) = \Delta G_S(AH) - \Delta G_S(A_OH)$ is neglected. An acidifying substituent, like CN, in AH which increases the gas acidity relative to A_OH by say 10 units, decreases the solvation of A^- by ~8.6 units in H_2O and ~6 units in DMSO.

It is well known that a substituent like CN that increases the charge delocalization in A^- causes a decrease of A^- solvation. The question why this decrease is smaller for dipolar aprotic solvents has been often answered on basis of an argument by Grunwald (19). The formation of A^- from AH leads to an increase of polarizability of A^- relative to AH because of the expansion of the delocalized electrons into a larger space. This increase of polarizability in A^- leads to an increase in dispersion forces between A^- and the solvent molecule. When solvent molecules with large polarizabilities (i.e. dipolar aprotic molecules) are present the increase of dispersion energy is larger than that for the small protic molecules like water. We believe that the higher dispersion energy for aprotic solvents is not the most important effect. Charge delocalization away from the oxygen of the phenoxide ion may be also considered as an increase of the effective radius of the charge center. The arguments presented in the preceeding section showed that the solvation by protic i.e. hydrogen bonding solvents like H_2O is very sensitive to ion radius, while that by dipolar aprotic solvents is not. Thus the factors involved in the lesser sensitivity of aprotic solvents to X^- radius increase may also be the applied to the lesser decrease of solvation by aprotic solvents in the presence of charge delocalization.

As pointed out in the preceeding section, the pyramidal DMSO is somewhat closer to protic solvents than acetonitrile or acetone. On this basis one would expect the slopes ρ for the latter two solvents to be less than the $\rho \approx 25$ observed for DMSO.

LITERATURE

1. A.M. Hogg and P. Kebarle, J. Chem. Phys. 43, 449 (1965); A.M. Hogg, R.N. Haynes and P. Kebarle, J. Am. Chem. Soc. 88, 28 (1966).
2. M.T. Bowers, D.H. Aue, H. Webb and R.T. McIver, Jr., J. Am. Chem. Soc. 93, 4314 (1971).
3. P. Kebarle, Ann. Rev. Phys. Chem. 28, 475 (1977).
4. D.H. Aue, M.T. Bowers, J.E. Bartmess and R.T. McIver, Jr., in "Gas Phase In Chemistry" M.T. Bowers Ed., Vol. 2, Academic Press.
5. S.G. Lias, J.F. Liebman, R. Lerin, J. Phys. Chem. Ref. Data in press.
6. P. Kebarle, in Modern Aspects of Electrochemistry Vol. 9 B.E. Conway and J.O.M. Bockris Ed., Plenum (1974).
7. I. Dzidic and P. Kebarle, J. Phys. Chem. 74, 1466 (1970).
8. W.E. Farneth, J.J. Brauman, J. Am. Chem. Soc. 98, 5546 (1976); W.N. Olmstead and J.J. Brauman, ibid., 99, 4219 (1978).
9. G. Caldwell, T. Magnera and P. Kebarle, J. Am. Chem. Soc. 106, 959 (1984).
10. A.J. Parker, Chem. Rev. 69, 1 (1964).
11. T. Magnera, G. Caldwell, J. Sunner, S. Ikuta and P. Kebarle. J. Am. Chem. Soc. 106, (in print) (1984).
12. W.R. Davidson and P. Kebarle, J. Am. Chem. Soc. 98, 6125 (1976).
13. S. Yamabe and K. Hirao, Chem. Phys. Leffers. 84, 598 (1982).
14. K. Hirao, S. Yamabe and M. Sano, J. Phys. Chem. 86, 2626 (1982).
15. J. Sunner and P. Kebarle, J. Am. Chem. Soc. 106, (in print) (1984).
16. T.B. McMahon and P. Kebarle, J. Am. Chem. Soc. 99, 2222 (1977).
17. M. Fujio, R.T. McIver, Jr., and R.W. Taft, J. Am. Chem. Soc. 103, 4017 (1981).
18. F.G. Bordwell, Pure and Appl. Chem. 49, 963 (1977).
19. E. Grunwald and E. Price, J. Am. Chem. Soc. 86, 4517 (1964).