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INTRINSIC (GAS-PHASE) BASICITIES AND STABILITY OF CHARGE-TRANSFER COMPLEXES IN SOLUTION

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The standard Gibbs energy changes for the formation of 1:1 charge-transfer complexes between molecular iodine and several bases in solution at 25·0 °C [ΔG^0_{I2}(soln)] were determined experimentally. The bases were 2,2,2-trifluoroethylamine, cyclopropylamine and 1,1,3,3-tetramethylguanidine. These [ΔG^0_{I2}(soln)] values, determined in *n*-heptane, and also that for the formation of the 1:1 complex between 2,2,2-trifluoroethanethiol and molecular iodine in dichloromethane, were found to follow with excellent precision the correlation equations linking ΔG^0_{I2}(soln) and the intrinsic (gas-phase) basicities of N(sp^3), N(sp^2) and S(sp^3) bases. These findings strongly support previous conclusions regarding the relationship between gas-phase and solution reactivity data. © 1997 by John Wiley & Sons, Ltd.

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Consider the formation of a 1:1 charge-transfer complex between an electron acceptor, A, and an electron donor, D, in solution in an 'inert' solvent, S:

$$\mathrm{A(soln)} + \mathrm{D\ (soln)} \rightleftharpoons \mathrm{A\cdots D(soln)} \qquad (1)$$

Mulliken's classical model of these interactions[1] treats the electronic wave function for the adduct A · · · D in its electronic ground state, ψ_{AD} as a linear combination of the wavefunctions for structures **I** and **II**, namely ψ_I and ψ_{II}.

$$\psi_{AD} = a\psi_I + b\psi_{II} \qquad (2)$$

$$\underset{\mathbf{I}}{\mathrm{AD}} \leftrightarrow \underset{\mathbf{II}}{\mathrm{A^-\ D^+}}$$

Structure **I** is stabilized by van der Walls interactions and is formally a 'no bonding' structure, whereas **II** is an ionic structure, characterized by the electron transfer from D to A. In general, in the ground state, the weight of structure **II** is much smaller than that of **I**, that is, $b^2/a^2 \ll 1$.

Some years ago,[2] we set out to investigate acid–base reactions taking place in solution in solvents other than water or other media able to disperse charges efficiently through hydrogen bonds. The reason for this was as follows. There are a number of experimental techniques[3] that allow the quantitative study of proton-transfer processes in the gas phase and the determination of the gas-phase basicities (*GB*) and proton affinities (*PA*) of neutral species B. For a given base B, these magnitudes are defined as $GB(\mathrm{B}) = -\Delta G_{\mathrm{H^+}}(\mathrm{g})$ and $PA(\mathrm{B}) = -\Delta H_{\mathrm{H^+}}(\mathrm{g})$, where $\Delta G_{\mathrm{H^+}}(\mathrm{g})$ and $\Delta H_{\mathrm{H^+}}(\mathrm{g})$ are the standard Gibbs energy and enthalpy changes, respectively, for the reaction

$$\mathrm{B(g)} + \mathrm{H^+(g)} \rightarrow \mathrm{BH^+(g)} \qquad (3)$$

The quantitative pattern of structural effects on gas-phase basicities is often different from that prevailing in protonation reactions in aqueous solution. This follows from the fact that, in the latter, the energetics of the reaction

$$\mathrm{B(aq)} + \mathrm{H^+(aq)} \rightarrow \mathrm{BH^+(aq)} \qquad (4)$$

depend heavily on the solvation of the onium ions, largely through charge dispersal to water solvent.[4]

We therefore sought solution systems wherein the general gas-phase pattern of reactivity would hold [it was known at that time that in some very specific cases the gas-phase and solution patterns are coincident:[2] (i) when solvation is not sterically hindered and the basic center and the number of acidic hydrogens are kept constant, as in the case of pyridinium ions,[5] and (ii) when extensive charge delocalization within the protonated base ensures an efficient 'internal solvation'[6]]. In view of the above, systems in which charge dispersal to the solvent would be minimized seemed to be prime candidates. Charge-transfer complexation reactions in 'inert' media, such as those defined by equation (1), were thus selected, molecular iodine, I_2, being the reference Lewis acid.

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Table 1. Experimental values of ΔG^0_{I2}(soln) and δGB for compounds **A**–**D**

Compound	ΔG^0_{I2}(soln)[a,b,c]	δGB[a,b,c,d]
2,2,2-Trifluoroethanethiol (**A**)	-0.57 ± 0.20[e,f]	-27.7[e]
2,2,2-Trifluoroethanamine (**B**)	-1.99 ± 0.11[g,h]	2.1[i]
Cyclopropylamine (**C**)	-4.51 ± 0.11[g,h]	11.0[i]
1,1,3,3-Tetramethylguanidine (**D**)	-5.96 ± 0.11[g,h]	38.4[i]

[a] Defined in the text.
[b] In kcal mol^{-1}.
[c] 1 kcal = 4.184 kJ.
[d] Corrected for changes in symmetry numbers following protonation, see text.
[e] From Ref. 7.
[f] Solvent is dichloromethane.
[g] This work.
[h] Solvent is *n*-heptane.
[i] See text and Ref. 8.

In the initial study we examined sulfur [S(sp^3)] and nitrogen [N(sp^2) and N(sp^3)] bases and found a series of good linear relationships between the structural effects on the Gibbs energy changes for reaction (5) in solution, ΔG^0_{I2}(soln), and the Gibbs energy changes (corrected for symmetry changes due to protonation) for reaction (3).

$$\mathrm{B(soln)} + \mathrm{I_2(soln)} \rightleftharpoons \mathrm{B\cdots I_2(soln)} \qquad K_c,\ \Delta G^0_{\mathrm{I2}}(\mathrm{soln}) \qquad (5)$$

The actual correlation equations found were as follows:

for S(sp^3) bases:

$$\Delta G^0_{\mathrm{I2}}(\mathrm{soln}) = (-3{\cdot}67 \pm 0{\cdot}09) - (0{\cdot}113 \pm 0{\cdot}007)\,\delta GB \qquad (6)$$

$$r^2 = 0{\cdot}960,\ n = 10,\ \mathrm{sd} = 0{\cdot}24\ \mathrm{kcal\ mol^{-1}}\ (1\ \mathrm{kcal} = 4{\cdot}184\ \mathrm{kJ})$$

for N(sp^3) bases:

$$\Delta G^0_{\mathrm{I2}}(\mathrm{soln}) = (-2{\cdot}29 \pm 0{\cdot}20) - (0{\cdot}162 \pm 0{\cdot}11)\,\delta GB \qquad (7)$$

$$r^2 = 0{\cdot}976,\ n = 6,\ \mathrm{sd} = 0{\cdot}25\ \mathrm{kcal\ mol^{-1}}$$

for N(sp^2) bases:

$$\Delta G^0_{\mathrm{I2}}(\mathrm{soln}) = (-0{\cdot}58 \pm 0{\cdot}08) - (0{\cdot}138 \pm 0{\cdot}04)\,\delta GB \qquad (8)$$

$$r^2 = 0{\cdot}980,\ n = 26,\ \mathrm{sd} = 0{\cdot}18\ \mathrm{kcal\ mol^{-1}}$$

In equations (6)–(8), δGB is the gas-phase basicity of the base relative to that of ammonia [that is, for base B, $\delta GB = \mathrm{GB(B)} - \mathrm{GB(NH_3)}$] and corrected for the eventual symmetry changes attending its protonation (note that, in general, the correction for changes in symmetry numbers following protonation leads to ΔGB values which are very close to the corresponding δPAs). All solution data were determined at 25·0 °C. Values of ΔG^0_{I2}(soln) for S(sp^3) bases were determined in CH_2Cl_2 and those for both N(sp^2) and N(sp^3) bases in *n*-C_7H_{16}. The experimental δGB values used in this work are either from us[7] or from studies carried

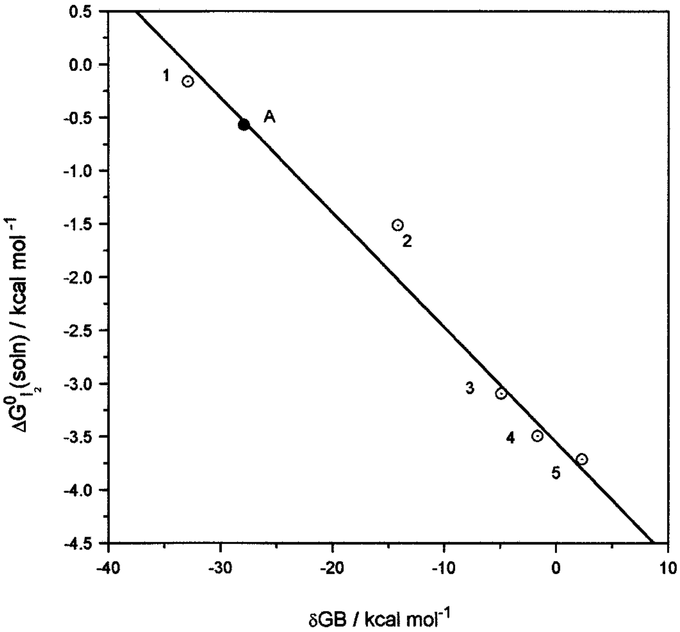

Figure 1. ΔG^0_{I2}(soln) vs δGB for S(sp^3) bases. The line is defined by equation (6). **A** is 2,2,2-trifluoroethanethiol. 1 = Hydrogen sulfide; 2 = ethanethiol; 3 = methyl sulfide; 4 = ethyl methyl sulfide; 5 = propyl sulfide.

out in Taft's laboratory and reported in several important compilations.[8]

These results are satisfactory. However, the variety of structures probed in this study was relatively limited. Thus, the S(sp^3) bases included H_2S, alkanethiols and cyclic and acylic thioethers, but none of these compounds bore a substituent able to induce a strong field effect. The same applied to the N(sp^3) bases. As regards the N(sp^2) bases, the data set involved 26 compounds, all of which were heterocyclic. It seemed to us that further study was needed in two directions: (i) the investigation of other families of bases having different basic centers and (ii) the critical testing of the applicability of equations (6)–(8) to other bases, not included in the initial study. Here, we present new results for the latter kind of experiments. Data for four different bases are reported: 2,2,2-trifluoroethanethiol (**A**), 2,2,2-trifluoroethananamine (**B**), cyclopropylamine (**C**) and 1,1,3,3-tetramethylguanidine (**D**).

Table 1 summarizes the experimentally determined ΔG^0_{I2}(soln) values for reaction (5) at 25·0 °C together with the corresponding δGB values. As in previous studies,[2] the equilibrium constants, K_c, were determined by means of standard UV–visible techniques.

The agreement between the experimental ΔG^0_{I2}(soln) values and those predicted by meaens of equations (6)–(8) is excellent. Figures 1 and 2 show the lines defined by these equations and also the points representing the new data. For the sake of clarity, only a few of the points previously used to determine the regression lines are shown. We felt that recalculating the regression lines with inclusion of the new values was of no interest at this point.

It is clear that the effect of the cyclopropyl and/or trifluoroethyl groups on the intrinsic basicities of thiols and amines is quantitatively reflected in the stabilities of the 1:1 charge-transfer complexes with iodine. It is also rewarding to see that **D**, a non-heterocyclic compound, both satisfies equation (8) to a high degree of approximation and further extends its range of validity.

Some important conclusions that can be drawn from the above are as follows:

1. The present results strongly support the validity of equations (6)–(8) and further extend their range of validity.
2. They also confirm the original hypothesis underlying these studies, namely that 'gas-phase-like' patterns of reactivity of a very broad scope can be found in solution, provided that the appropriate solvents are used.
3. Although the relative weight of the zwitterionic structures **II** (A^- D^+) is generally small in charge-transfer

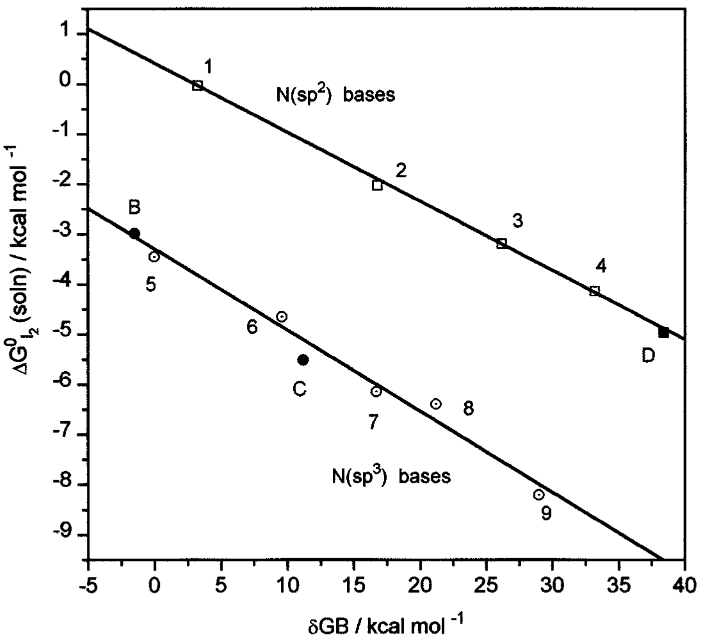

Figure 2. ΔG^0_{I2}(soln) vs δGB for N(sp^3) (circles) and N(sp^2) (squares) bases. The lines are defined by equations (7) and (8). In the figure they are shifted downwards and upwards, respectively, by 1 kcal mol^{-1}. **B** = 2,2,2-trifluoroethanamine; **C** = cyclopropylamine; **D** = 1,1,3,3-tetramethylguanidine. 1 = 3-Nitropyridine; 2 = pyridine; 3 = *N-tert*-butylimidazole; 4 = dimethylaminopyridine; 5 = ammonia; 6 = methylamine; 7 = dimethylamine; 8 = trimethylamine; 9 = quinuclidine

complexes in their electronic ground states, it is clear that even this small contribution is able to make the stability of large families of complexes cleanly mirror the intrinsic basicity of the electron donors.

4. As pointed out by a referee, steric effects on the stability of the charge-transfer complexes examined in these studies are generally small. Note, however, that the datum for trimethylamine (point 8, Figure 2) suggests some degree of steric destabilization.
5. Molecular iodine is a typical 'soft' acid in the sense of Pearson[9] whereas the proton is a 'hard' acid. It is clear that these results indicate that, within families of compounds having a common basic center, structural effects on the reactivities towards these two acids are similar.

We have recently examined the case of 1:1 hydrogen bonding complexes of neutral species in the gas phase[10] and found that the quantitative pattern of structural effects of donors and acceptors on their stability is the same as found in solvents such as tetrachloromethane or cyclohexane. All these results taken together strongly suggest that for many processes taking place in environments in which bulk water and/or other species leading to strong charge-dispersal through hydrogen bonding are absent, gas-phase thermodynamic data are possibly the choice descriptors of structural effects.

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