Re-evaluation of the inductive effect in isolated molecules and in solution

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ABSTRACT: The classical concept of inductive effect based originally on dissociation constants in water was revisited on isolated molecules in the gas phase. It then has a strict thermodynamic meaning of $\Delta H^o(g)$ of an isodesmic reaction and can be calculated separately in the neutral molecules of acids (bases) and in anions (cations). Eight different reactions were investigated in which tradition assumes a purely inductive effect. Quantitative estimation was based on the known gas-phase enthalpies of ionization, $\Delta_{ion}H^o(g)$, and gas-phase enthalpies of formation, $\Delta_f H^o(g)$; some lacking values of the latter were substituted by calculations at the MP2/6–31+G** or RHF/6–31+G** level. Substituent effects in neutral molecules are not negligible, particularly in smaller molecules, but are qualitatively different from the common scale of inductive effect and cannot at present be described in terms of any simple theory. The concept of inductive effect is to be reserved just for the energy difference between an ion and the respective neutral molecule. It can be modeled as the energy of interaction between the given substituent and a positive or negative charge but it is quantitatively predicted in terms of electrostatics (Kirkwood–Westheimer theory) only with some considerable disagreements. In water, this effect is strongly attenuated, differently in different classes of compounds; this attenuation can be in a qualitative accord with the electrostatic theory. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: electrostatic effects; inductive effects; substituent effects; acidity; basicity

INTRODUCTION

The inductive effect (I-effect) has represented one of the basic terms of theoretical chemistry, particularly within the framework of the classical English school.[1–3] This view is maintained in most contemporary textbooks,[4] although some of them prefer the term field effect,[4a] or give somewhat less place to the whole problem.[4d,e] Development of this concept has proceeded mainly along two lines. On the one hand, effects of individual substituents were quantitatively estimated[5–8] and expressed by a scale of constants denoted σ_I or σ_F; good evidence was obtained that they remain proportional and can be transferred from one reaction to another.[7,9,10] On the other hand, simplified theories were advanced which either express the I-effect in terms of electrostatic repulsion or attraction,[11,12] or describe its propagation along the bonds[13] with a possible similarity to an electric network.[14] Pros and cons of the two theories have been discussed,[15,16] but recently the opinion prevails that they should be regarded only as two very approximate models.[17,18]

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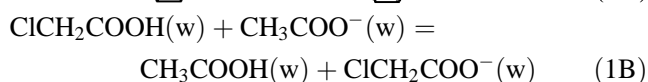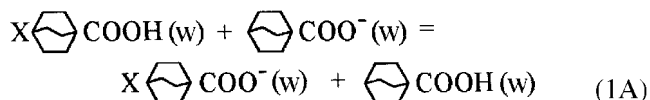E-mail: uochb@uochb.cas.cz

In this paper, we call attention to another aspect. Although the derived values of σ_F have been applied also to gas-phase reactions,[19–21] most of the classical examples of the I-effect concern ionization equilibria in water and the effect is observed as a difference in pK values of the substituted and unsubstituted acid or base. In thermodynamic terms, this difference can be expressed as the reaction Gibbs energy $\Delta_1 G^o$ (or reaction enthalpy $\Delta_1 H^o$) of an isodesmic reaction, Eqn. (1), where X is a substituent, Y a functional group and G a connecting skeletal group:

$$X\text{–}G\text{–}YH(w) + H\text{–}G\text{–}Y^-(w)$$
$$= H\text{–}G\text{–}YH(w) + X\text{–}G\text{–}Y^-(w) \qquad (1)$$
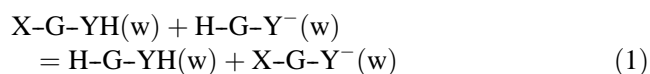
Equation (1) may be regarded as a new definition[17] of the I-effect in chemical thermodynamics. Its merit is that it is based on observable and measurable quantities which may be derived on a suitable model system. Commonly, the term I-effect is understood somewhat differently: according to textbook definitions[4] it is related mostly to electron distribution (not observable) or still worse to the 'mode of transmission' (not observable, and strictly not existing). A new definition would perhaps require a new term but a suitable word has not yet been found.[17,18] Of course, Eqn. (1) relates to substituent effects of any kind. In order to decide which effect is considered as purely

inductive, the skeletal group G must possess certain properties which have not been defined exactly. Generally, it is assumed that G should contain no double bonds (at least not a conjugated system) to exclude any resonance effects, and should be sufficiently large and rigid to exclude any direct contact between X and Y (steric effect). Excellent model systems are derivatives of bicyclo[2.2.2]octane,[20–22] as for instance in Eqn. (1A), but even a mere CH_2 group may be sufficient[6] as in the classical example, chloroacetic acid, in Eqn. (1B):

$$X\hexagon COOH\,(w) + \hexagon COO^-\,(w) =$$
$$X\hexagon COO^-\,(w) + \hexagon COOH\,(w) \qquad (1A)$$

$$ClCH_2COOH(w) + CH_3COO^-(w) =$$
$$CH_3COOH(w) + ClCH_2COO^-(w) \qquad (1B)$$

The whole reasoning applies only to the I-effect on ground-state properties. Extension to other properties, e.g. to NMR spectra,[5b] is possible but must be based on empirical correlations.[9] When $\Delta_1 G^\circ$ is to be interpreted in terms of structure, the structural parameters relate to isolated molecules. This has two defects: first, $\Delta_1 G^\circ$ includes an unknown contribution from the solvation, and second, it is only a difference between the effects in the acid and in the anion. The goal of this paper is re-evaluation of the I-effect for isolated molecules. First, we shall exploit the published data on acid–base equilibria in the gas phase[19–21,23,24] to separate the I-effect from the contribution of solvent. Second, we shall evaluate separately the effect in the acid (base) and in the anion (cation) by means of isodesmic reactions[25–27] based on the known enthalpies of formation. The general programme has been outlined[27] and applied already to various steric effects,[28] buttressing effect[29] and hyperconjugation.[30] It is not without predecessors;[25] however,

it exploits the known principles in a systematic way. There is a particular feature of the I-effect that it is generally valid and quantitatively proportional in various series.[7,9,10] Therefore, it is necessary to investigate several model systems, particularly those defined by Eqns (1A) and (1B), in addition to the acidities of the acids also the basicities of similar bases. For the compounds under consideration, experimental gas-phase acidities and basicities are available[20,21,23,24] but only few gas-phase enthalpies of formation.[31] Hence the latter were replaced by *ab initio* energies at an MP2/6–31+G** or RHF/6–31+G** level. According to our recent experience,[32] even the RHF/6–31G** calculations were recently found sufficient for such purposes, not worse than some more sophisticated procedures.

RESULTS AND DISCUSSION

Ionization in the gas phase

The I-effect in the gas phase is generally defined by Eqn. (2), particular examples are Eqns (2A) and (2B) for carboxylic acids or Eqns (2C) and (2D) for bases. In the gas phase, the enthalpies $\Delta_2 H^\circ$ are preferable to Gibbs energies[9] $\Delta_2 G^\circ$ but mostly the two are equal except for the symmetry factors[26] which should be not included in the substituent effect. A note is still required concerning the reference compound, i.e. compound without susbtituent. In solution, Eqn. (1), a hydrogen atom has been always used as reference substituent. In the gas phase and particularly in smaller molecules, it may be more convenient to use a methyl group. Its inductive effect is equal to zero[19] and its polarizability may be nearer to the polarizability of the variable substituent. This choice was applied in Eqn. (2B) and some other reactions involving smaller molecules (Table 1). For larger molecules as in

Table 1. Thermodynamic quantities of isodesmic reactions pertinent to the inductive effect (kJ mol^{-1})

	Substituted compound	Equations	Substituent	Reference	Acid (base) $\Delta_3 H^\circ(g)^a$	Anion (cation) $\Delta_4 H^\circ(g)^b$	Acidity (basicity)	
							$\Delta_2 H(g)^c$	$\Delta_2 G^\circ(w)^d$
	Acids							
1	$ClCH_2COOH$	(2B)–(4B)	Cl	CH_3	15.5	−30.5	−46.0	−11.5
2	CF_3CH_2OH	—	CF_3	CH_3	20.0	−46.5	−66.5	−20.0
3	$4\text{-}FC_8H_{12}COOH$	(2A)–(4A)	F	H	3.5^e	−19.9	−23.4	−3.0
4	$3\text{-}NO_2C_6H_4OH$	—	NO_2	H	7.9^f	−52.3^f	−60.2	−9.2
	Bases							
5	$NCCH_2N(CH_3)_2$	(2D)–(4D)	CN	CH_3	−6.1	69.5	75.6	32.2
6	$4\text{-}NCC_8H_{12}CN$	(2C)–(4C)	CN	H	8.6	41.7	33.1	—
7	$3\text{-}NO_2C_6H_4NH_2$	—	NO_2	H	−1.8^f	55.5^f	57.3	12.3
8	$3\text{-}CNC_5H_4N$	—	CN	H	6.1	59.1	53.0	23.3

^{a} MP2 energies calculated in this work unless stated otherwise.
^{b} Sum of $\Delta_3 H^\circ(g)$ of the acid or base (calculated or experimental) and of the experimental acidity or basicity $\Delta_2 H^\circ(g)$.
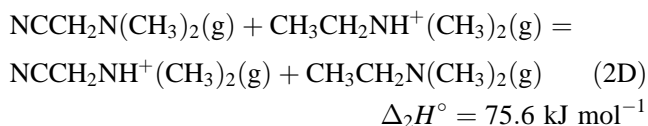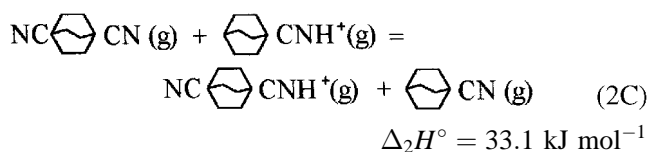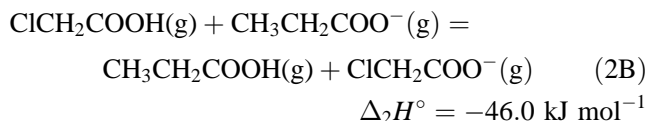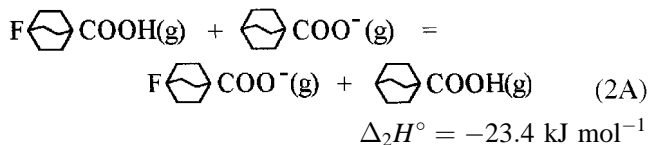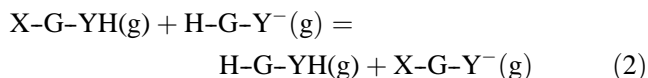^{c} Experimental values from Refs. 19, 20, 23 and 24.
^{d} Experimental values from Ref. 34.
^{e} Calculated at the RHF level.
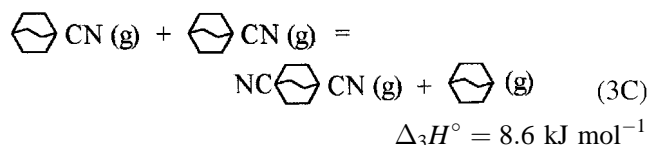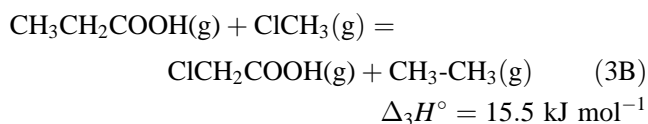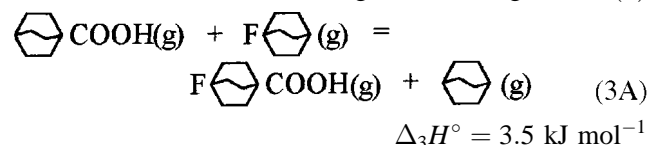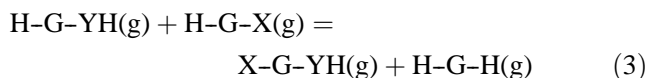^{f} Experimental values, based on $\Delta_f H^\circ_{298}(g)$ from Ref. 31.

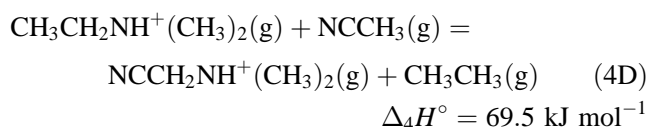Eqn. (2A), this choice is unimportant since the polarizability effects are negligible.[19]

$$X\text{–}G\text{–}YH(g) + H\text{–}G\text{–}Y^-(g) =$$
$$H\text{–}G\text{–}YH(g) + X\text{–}G\text{–}Y^-(g) \qquad (2)$$

$$F\langle\bigcirc\rangle COOH(g) + \langle\bigcirc\rangle COO^-(g) =$$
$$F\langle\bigcirc\rangle COO^-(g) + \langle\bigcirc\rangle COOH(g) \qquad (2A)$$
$$\Delta_2 H^\circ = -23.4 \text{ kJ mol}^{-1}$$

$$ClCH_2COOH(g) + CH_3CH_2COO^-(g) =$$
$$CH_3CH_2COOH(g) + ClCH_2COO^-(g) \qquad (2B)$$
$$\Delta_2 H^\circ = -46.0 \text{ kJ mol}^{-1}$$

$$NC\langle\bigcirc\rangle CN\,(g) + \langle\bigcirc\rangle CNH^+(g) =$$
$$NC\langle\bigcirc\rangle CNH^+(g) + \langle\bigcirc\rangle CN\,(g) \qquad (2C)$$
$$\Delta_2 H^\circ = 33.1 \text{ kJ mol}^{-1}$$

$$NCCH_2N(CH_3)_2(g) + CH_3CH_2NH^+(CH_3)_2(g) =$$
$$NCCH_2NH^+(CH_3)_2(g) + CH_3CH_2N(CH_3)_2(g) \qquad (2D)$$
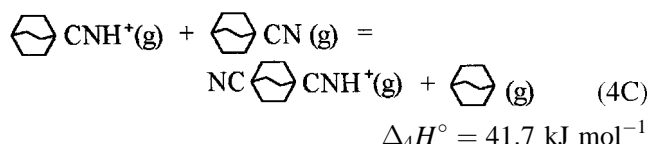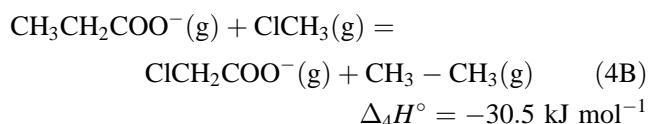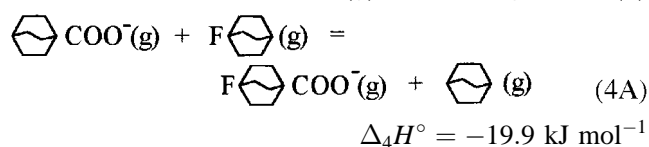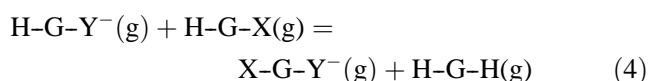$$\Delta_2 H^\circ = 75.6 \text{ kJ mol}^{-1}$$

In order to separate the effects in the acid and in the anion, let us construct the isodesmic reaction, Eqn. (3), in which the substituted acid is synthesized from two mono derivatives. The reaction enthalpy, $\Delta_3 H^\circ$, may be viewed as the substituent effect of the group X on the group Y or *vice versa*. Equations (3A)–(3D) are examples in which the effect should be purely inductive.

$$H\text{–}G\text{–}YH(g) + H\text{–}G\text{–}X(g) =$$
$$X\text{–}G\text{–}YH(g) + H\text{–}G\text{–}H(g) \qquad (3)$$

$$\langle\bigcirc\rangle COOH(g) + F\langle\bigcirc\rangle(g) =$$
$$F\langle\bigcirc\rangle COOH(g) + \langle\bigcirc\rangle(g) \qquad (3A)$$
$$\Delta_3 H^\circ = 3.5 \text{ kJ mol}^{-1}$$

$$CH_3CH_2COOH(g) + ClCH_3(g) =$$
$$ClCH_2COOH(g) + CH_3\text{-}CH_3(g) \qquad (3B)$$
$$\Delta_3 H^\circ = 15.5 \text{ kJ mol}^{-1}$$

$$\langle\bigcirc\rangle CN\,(g) + \langle\bigcirc\rangle CN\,(g) =$$
$$NC\langle\bigcirc\rangle CN\,(g) + \langle\bigcirc\rangle(g) \qquad (3C)$$
$$\Delta_3 H^\circ = 8.6 \text{ kJ mol}^{-1}$$

$$CH_3CH_2N(CH_3)_2(g) + NCCH_3(g) =$$
$$NCCH_2N(CH_3)_2(g) + CH_3CH_3(g) \qquad (3D)$$
$$\Delta_3 H^\circ = -6.1 \text{ kJ mol}^{-1}$$
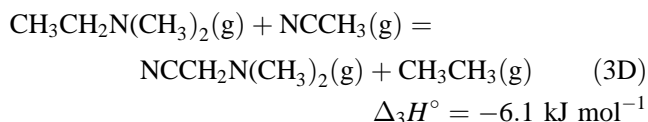
The values of $\Delta_3 H^\circ$ could be in some cases calculated from the published[31] enthalpies of formation in the gas

phase, $\Delta_f H^\circ(g)$, of all species involved. Note that only experimental $\Delta_f H^\circ(g)$ are needed. Lacking values have often been estimated from the additivity principle with a reasonable approximation[31] but they are not sufficiently precise for our present purpose. If the additivity principle were valid exactly, all $\Delta_3 H^\circ$ would be zero. When $\Delta_3 H^\circ$ were not available, they were replaced by the sum of calculated MP2 energies, $\Delta_3 E$(MP2). All values are listed in Table 1, column 5, together with the experimental values of $\Delta_2 H^\circ$ (column 7). With respect to the general validity of the I-effect, we have included in this table as diverse reactions as possible: acidities of carboxylic acids of the acetic acid series (line 1) and bicyclooctane series (line 3), acidities of alcohols (line 2), basicities of substituted methylamines (line 5) and substituted bicyclooctanecarbonitriles (line 6). Also included were aromatic *meta* derivatives with acceptor substituents for which we have evidence[33] that only the inductive effect is operative: phenols (line 4), anilines (line 7) and pyridines (line 8).

Determining the substituent effect in the anion is more complex. This is defined by the isodesmic reaction, Eqn. (4); particular examples are Eqns (4A)–(4D). Its value is obtainable through a thermodynamic cycle as $\Delta_4 H^\circ = \Delta_2 H^\circ + \Delta_3 H^\circ$.

$$H\text{–}G\text{–}Y^-(g) + H\text{–}G\text{–}X(g) =$$
$$X\text{–}G\text{–}Y^-(g) + H\text{–}G\text{–}H(g) \qquad (4)$$

$$\langle\bigcirc\rangle COO^-(g) + F\langle\bigcirc\rangle(g) =$$
$$F\langle\bigcirc\rangle COO^-(g) + \langle\bigcirc\rangle(g) \qquad (4A)$$
$$\Delta_4 H^\circ = -19.9 \text{ kJ mol}^{-1}$$

$$CH_3CH_2COO^-(g) + ClCH_3(g) =$$
$$ClCH_2COO^-(g) + CH_3 - CH_3(g) \qquad (4B)$$
$$\Delta_4 H^\circ = -30.5 \text{ kJ mol}^{-1}$$

$$\langle\bigcirc\rangle CNH^+(g) + \langle\bigcirc\rangle CN\,(g) =$$
$$NC\langle\bigcirc\rangle CNH^+(g) + \langle\bigcirc\rangle(g) \qquad (4C)$$
$$\Delta_4 H^\circ = 41.7 \text{ kJ mol}^{-1}$$

$$CH_3CH_2NH^+(CH_3)_2(g) + NCCH_3(g) =$$
$$NCCH_2NH^+(CH_3)_2(g) + CH_3CH_3(g) \qquad (4D)$$
$$\Delta_4 H^\circ = 69.5 \text{ kJ mol}^{-1}$$

When $\Delta_2 H^\circ$ is an experimental value while a calculated energy has been substituted for $\Delta_3 H^\circ$, the resulting $\Delta_4 H^\circ$ is a mixed value, theoretically not pure. However, our experience with such values was good.[28a] Even in this paper, we did not obtain completely satisfactory results when we calculated also the energies of the anions or cations at the same level as in the case of neutral molecules. These calculations can be tested since the calculated reaction enthalpies $\Delta_2 H^\circ$ can be directly

Table 2. Comparison of calculated and experimental reaction enthalpies (kJ mol^{-1})

Reaction	Calculated			Exp.[a]
	3–21G	6–31+G**	MP2/6–31+G**	
Isodesmic reactions				
ClCH$_2$COOH, Eqn. (3B)	30.4	24.7	15.5	16.2
CF$_3$CH$_2$OH	23.3	23.1	27.1	8.0
Ionization reactions				
ClCH$_2$COOH, Eqn. (2B)	−72.9	−57.2	−50.9	−46.0
CF$_3$CH$_2$OH	−110.0	−94.5	−91.8[b]	−66.5
4-FC$_8$H$_{12}$COOH, Eqn. (2A)	−22.2	−22.2	—	−23.4
NCCH$_2$N(CH$_3$)$_2$, Eqn. (2D)	79.9	85.8	77.4	75.6
4-NCC$_8$H$_{12}$CN, Eqn. (2C)	32.1	33.0	30.3	33.1
3-CNC$_5$H$_4$N	59.6	63.5	—	53.0

[a] From Refs 19, 20, 23 and 24.
[b] According to G2(MP2) calculations,[35] the value of −76.1 kJ mol^{-1} would be obtained; isodesmic reactions were not investigated.

compared with the experimental values of relative acidities or basicities. Table 2, lower part, reveals that the agreement is bad. It evident that calculated energies of ions, particularly for anions, are at this level less reliable than those for neutral molecules. The latter could be tested only on two examples (Table 2, upper part). In the case of Eqn. (3B), agreement with experiment is good and improves systematically with a more sophisticated procedure. In the case of 2,2,2-trifluoroethanol, the basis set seems to be not sufficient (Table 2, footnote b). The whole procedure just described was applied several times to substituent effects of various kind:[27–30] while the principle was the same, the experimental approach was different according to which quantities were already known.

The data in Table 1 must be treated with caution since the experimental enthalpies of formation are of different accuracy and the calculations need not always be dependable. Nevertheless, even when we restrict discussion to the values greater than 5 kJ mol^{-1}, the following conclusions are evident:

1. The substituent effect $\Delta_3 H°$ in the neutral molecule of an acid or base is not always negligible but can be hardly interpreted in a simple way. It is evidently small in larger molecules (derivatives of benzene, pyridine and [2.2.2]bicyclooctane), but might attain (not always) more than 10 kJ mol^{-1} when the substituent and functional group are separated only by one methylene group. Nor is the sign of the effect predictable with certainty. It is mostly positive (destabilizing), particularly when the substituent and functional group are identical or both are electron attracting. This generalization is valid also for the OH group when it is regarded as electron attracting. In contrast, the NH$_2$ and N(CH$_3$)$_2$ yield a negative $\Delta_3 H°$. In no case is there any relation between $\Delta_3 H°$ and the common inductive effect as quantified, e.g., by the constants σ_I. Substituent effects in the ground state of neutral

molecules have been generally little investigated;[26,36] the most recent review on gas-phase reactions[37] deals with equilibria of ionic reactions but only with kinetics in the case of neutral species. Some destabilizing by the inductive effect of two electron-attracting groups was revealed,[26] besides a rather strong stabilizing effect[36] (called φ interaction) between an electron-attracting and a polarizable group. For the latter effect, there is no example among our reactions.

2. The substituent effect $\Delta_4 H°$ in the ions is much greater and more readily understandable. It is negative (stabilizing) in anions and positive in cations since all our substituents are electron attracting. It cannot be related to the polarizability of substituents:[26] in this case it should alway be negative. The best qualitative description is still in terms of a pole–dipole electrostatic interaction according to the classical Kirkwood–Westheimer equation,[11] Eqn. (5), where μ is the substituent dipole, r its distance from the pole and θ the angle between these two vectors; the effective permittivity ε_{ef} is taken as unity in the gas phase

$$\Delta G° = -N_A e\mu \cos\theta / r^2 \varepsilon_{ef}(4\pi\varepsilon_0) \qquad (5)$$

However, a quantitative prediction by means of Eqn. (5) fails in many cases. First, the effect of the angle θ is overestimated.[15] Second, a reliable estimation of ε_{ef} is impossible in solution and in the gas phase Eqn. (5) fails completely since it would require ε_{ef} to be smaller than unity.[17]

3. Substituent effect on the acidity or basicity, $\Delta_2 H°$, is controlled mainly by the effect in the ion, $\Delta_4 H°$, and only slightly or moderately influenced by the effect in the undissociated molecule, $\Delta_3 H°$. The effect of the latter is greatest in the case of acids with a small molecule (lines 1 and 2 in Table 1). The acid-strengthening effect in these molecules is due to two thirds from the effect in the anion and one third from

the effect in the undissociated acid. In certain bases, these two effects may even be opposite (lines 6 and 8 in Table 1) but $\Delta_4 H°$ prevails strongly.

Ionization in solution

The inductive effect was investigated here on eight reactions of isolated molecules. However, most of the literature data concern ionization in solution, mostly in water. Separate evaluation of this effect in the ions and in undissociated molecules, similarly as in Eqns (3) and (4), would be possible only in few cases and will be abandoned at present. However, many relative dissociation constants are available,[34] which can be substituted into Eqn. (1), and then compared with the gas-phase ionization, Eqn. (2). Comparison was carried out in terms of enthalpies in the gas phase, $\Delta_2 H°(g)$, and Gibbs energies in water $\Delta_2 G°(w)$.

Figure 1 reveals two pertinent features: (a) substituent effects are smaller in solution (attenuation) and (b) this attenuation is different in different classes of compounds— all points are not situated near one line. [There is no closer linear dependence between $\Delta_2 G°(w)$ and $\Delta_2 H°(g)$ even within these separate classes: the lines in Fig. 1 are purely formal regression lines.] Attenuation is a well known phenomenon; recently it was evaluated for several classes of compounds in an indirect way,[20] viz. through the correlations with the constants σ_F. Remarkably, some of the differences can be qualitatively interpreted in terms of Eqn. (5) and of the effective permittivity[11,15] ε_{ef}. When the molecule is placed in a spherical or ellipsoidal cavity,[15] where the charge and dipole are situated at fixed distances[38] from its surface, then in larger molecules this fixed distance is relatively smaller with respect to the molecule size. The charge is less screened by the molecule and the estimated ε_{ef} and the attenuation are greater (aromatic and cyclic compounds). The difference between acids and bases has not yet been explained. In our opinion, an *ad hoc* interpreta-
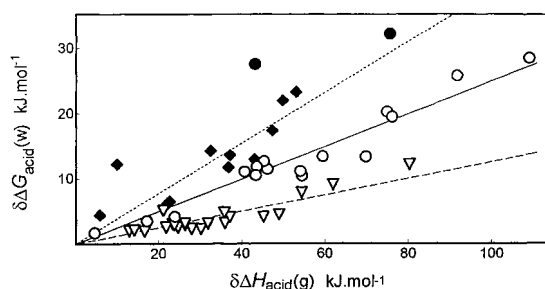
tion is possible that the positive charge in the cations is more deeply situated in the molecular cavity than the negative charge in the anions: then the assumption of a fixed distance from the surface[38] cannot be transferred from the acids to the bases. On the whole, one can conclude that the observed effects of solvation are in reasonable accord with the electrostatic theory and with Eqn. (5). In our opinion, this does not change the general appraisal of this theory, that it can be applied only in a semiquantitative way, with a moderate success and with many assumptions.

CONCLUSIONS

The classical concept of the I-effect together with the scale of inductive substituent constants is applicable to entities containing a charged atom, i.e. to ions and strongly polar transition states. Substituent effects in the ground state of uncharged molecules are relatively weak and are governed by other, not well understood and not exactly evaluated, effects. It follows that the effect on acidity must not be attributed to electron distribution in the acid molecule and represented by the popular equations showing shifts of electrons by arrows[3] (e.g. in chloroacetic acid). A similar picture would be acceptable for the anion and the electron shifts should start better from the negative charge than from the substituent. The I-effect can be qualitatively described by pole–dipole interactions, both in the isolated molecule and in solution, although a quantitative description within the framework of the Kirkwood–Westheimer theory fails.

CALCULATIONS

Ab initio calculations for all compounds involved in the reactions of Table 1 were performed using the Gaussian 94 program[39] at the RHF/6–31+G** and MP2/6–31+G** levels. Vibrational analysis was carried out in all cases: all structures belong to an energy minimum. All calculations were carried out at variable levels as shown in the examples of Table 2. The results are given in terms of isodesmic reactions (Table 1); comparison with experiments was carried out in the same way (Table 2). Calculations of $\Delta H°_{298}$ carried out in some cases did not improve the agreement with experiments.

Figure 1. Comparison of the relative acidities or basicities (absolute values) in the gas phase and in water. ○, Derivatives of acetic acid; ▽, aromatic, cyclic and bicyclic carboxylic acids; ●, derivatives of methylamine; ◆, aromatic, cyclic and bicyclic amines. Experimental data from Refs 19, 20, 23, 24 and 34

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