Resonance energy in benzene and ethene derivatives in the gas phase as a measure of resonance ability of various functional groups †

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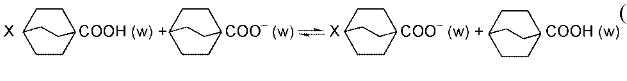
Three sets of isodesmic reactions in the gas phase were constructed in which a variable functional group is transferred from a saturated to an unsaturated hydrocarbon residue: methyl→phenyl, *tert*-butyl→phenyl, ethyl→ethenyl. Reaction enthalpies, obtained either from the known enthalpies of formation or by calculations at an MP2 or DFT level, were considered as new possible scales of resonance effect of these functional groups; in the case of charged groups ($CHOH^+$, NO_2H^+, O^-, COO^-, *etc.*) it is the only way to estimate their effects reliably. One scale was also transferred from the gas phase into aqueous solution by adding the Gibbs energies of solvation of all compounds involved. All scales are only partly parallel to the common scales of substituent constants $\sigma_R{}^\circ$, $\sigma_R{}^+$ or $\sigma_R{}^-$. Some particular deviations were specified: stabilizing homoconjugation of the CH_2X substituents with the benzene π-electrons, or stabilizing interaction of polar groups with the *tert*-butyl group. However, most of the deviations are of an unknown nature: they are not due to solvation which affects the resonance energy rather little, and are only slightly influenced by the polarizability of the phenyl group. One cause of the deviations could be that all σ_R values have been defined on models involving ions.

Introduction

Resonance is undoubtedly a useful qualitative concept predicting a relatively low energy of certain molecules only on the basis of their structural formulas. Its quantitative estimation in typical examples (*e.g.* in benzene) compares the energy of a real molecule with an anticipated energy for a model molecule: problems arise about the structure of this model as explained even in most contemporary textbooks.[1] Within the framework of correlation analysis, another approach was created[2] for evaluating relative resonance energy of various groups when they are bonded onto a constant hydrocarbon residue. Usually this is a phenyl group which must also have another functional group as probe. In this approach, reactivities of two similar systems must be compared, one with resonance (*e.g.* a *para* substituted benzoic acid) and one without resonance with an approximately equal inductive effect (*e.g.* 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid). Resonance of a certain group is expressed on a conventional scale by the resonance constant σ_R within the framework of Taft's DSP (Dual Substituent Parameter) treatment.[2,3] The DSP system has been broadly used to correlate various properties of diverse molecules,[2–4] although the results were not always satisfactory.[5]

A serious objection is that resonance depends on the choice of the probe group, *e.g.* COOH, OH, NH_2, C^+Me_2. The dependence of the effective σ_R on electron demand of the probe group was thoroughly investigated.[3,6] As an extreme case, a sliding scale of σ_R was taken into consideration[6c] but more commonly several scales of constants have been settled[3,6] ($\sigma_R{}^\circ$, $\sigma_R{}^+$, $\sigma_R{}^-$, σ_D). The choice in a particular case may not be unambiguous and was criticized as rather arbitrary.[5] Another problem is the correct scaling of the inductive effect,‡ affecting the resulting σ_R.[7] In terms of thermodynamics, σ_R evaluation involves subtraction of ΔG° values of the two isodesmic reactions, for instance eqns. (1) and (2), scaled to a common scale.

$$\text{4-X-}C_6H_4COOH(w) + C_6H_4COO^-(w) \rightleftharpoons \text{4-X-}C_6H_4COO^-(w) + C_6H_4COOH(w) \quad (1)$$



(2)

Estimation of a single value of σ_R thus requires four experimental relative p*K* values, altogether eight molecules. Another shortcoming is restriction to solutions in water or to aqueous solvents. Water as solvent may profoundly influence the apparent resonance, and the concept of Specific Substituent Solvation Assisted Resonance (SSSAR) was introduced.[8]

Further scales of resonance effects were suggested, essentially empirical in character. The values of $\sigma_R{}^\circ$ were related[9] to the intensity of the skeletal frequency of the benzene nucleus denoted ν_{16a} and ν_{16b} (at 1600 and 1585 cm^{-1}) in benzene monoderivatives C_6H_5X. A possible inductive effect was neglected. In a scale based on ^{19}F NMR shifts of substituted fluorobenzenes

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† Table S1 giving HF energies, MP2 energies and ΔH°_{298} of 33 derivatives of ethane C_2H_5X and 33 derivatives of ethene $CH_2{=}CHX$ is available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b003073m/

‡ Previous evaluation of the inductive effect was often critical for the resulting calculated resonance effect, and may also depend on how the inductive effect is exactly defined. The problem was recently discussed in detail, ref. 25. In our concept, we avoid any not observable phenomena as "mode of transmission" and define the inductive effect simply as observed substituent effect in saturated systems. Then the word "inductive" appears inappropriate but a better has not yet been suggested, ref. 25.

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XC_6H_4F, shifts of the *para* and *meta* derivative were subtracted.[10] A quantum chemical approach was suggested,[11] defining the constant $\sigma_R{}^\circ$ from the π-electron population on the two carbon atoms in substituted ethenes $XCH=CH_2$. All the scales reveal a similar sequence, although the correlation is not perfect: correlation coefficients between the three last mentioned scales were found[11b] to be 0.985, 0.981 and 0.970, respectively.

In our opinion, the most fundamental scale should be related to the energies of isolated molecules, not to solution properties, should be restricted to thermodynamics, and should not involve any particular probe group except the unsaturated hydrocarbon residue itself. In this paper, we examine three such scales based on the reaction enthalpies of isodesmic reactions,[12] eqns. (3)–(5).

$$CH_3X(g) + C_6H_6(g) \rightleftharpoons XC_6H_5(g) + CH_4(g) \quad (3)$$

$$(CH_3)_3CX(g) + C_6H_6(g) \rightleftharpoons XC_6H_5(g) + (CH_3)_3CH(g) \quad (4)$$

$$C_2H_5X(g) + CH_2{=}CH_2(g) \rightleftharpoons XCH{=}CH_2(g) + C_2H_6(g) \quad (5)$$

In equations (3)–(5), resonance can occur only in the unsaturated molecules on the right side. The reaction enthalpies, Δ_3H°–Δ_5H°, express more or less exactly resonance in these molecules arising by joining the groups X and C_6H_5 or C_2H_3. However, minor contributions of other effects can be also considered, to different extents in eqns. (3)–(5):

Eqn. (3), written from right to left and based on simple STO3G calculations, has already been used in some cases for defining the "stabilization energy".[12b] This term means essentially resonance energy with a reversed sign. The concept of these authors[12b] was virtually the same as ours, although the terminology was different. Eqn. (3) may not be an ideal model since in addition to resonance some part of the reaction enthalpy Δ_3H° may be explained by the greater polarizability of phenyl compared with methyl. The main merit of eqn. (3) is that Δ_3H° can be calculated for many groups X from the experimental enthalpies of formation,[13] Δ_fH°, of all molecules present.

Eqn. (4) involving a more polarizable *tert*-butyl group would be possibly a better model but only a limited number of Δ_fH° values are available. The same applies to eqn. (5) in which many of the substituted ethenes are unstable or even cannot be prepared. For this reason, we have replaced experimental enthalpies Δ_5H° by *ab initio* calculations of HF or MP2 energies or enthalpies ΔH°_{298} (the latter calculated from MP2 energies using standard programs for statistical thermodynamics[14]).

Resonance effects defined by these equations are to be considered as observable quantities, based on experiments and independent of any solvent effects. Our intention was to compare them with the scales commonly used and to examine to what extent they correspond to the common concept of resonance substituent effect. We did not expect identity of all scales—mainly because in our models a polar probe group was lacking—but we believed that our scales will be of importance as fundamental reference.

Results and discussion

Calculations

Ab initio calculations were performed by means of the GAUSSIAN94 program[14] at the levels RHF/6-31+G(d,p), MP2/6-31+(d,p), for some molecules also B3LYP/6-311+G(3df,2pd)//MP2/6-31G(d,p). Vibrational analyses were carried out in all cases: all structures are at energy minimum. Enthalpies at 298 K were calculated from MP2 energies with the same program.[14] The values of *E*(RHF), *E*(MP2) and ΔH°_{298} of the molecules C_2H_5X and $CH_2{=}CHX$ are listed in Table S1 (Supplementary data), some values of *E*(B3LYP) are given in the footnotes to Table S1.

Resonance energies in the gas phase

We have to deal with resonance energies of three types, defined as reaction enthalpies of the isodesmic reactions, which may possibly serve as new scales of resonance effects (Table 1).

Δ_3H° defined by eqn. (3) was obtained as a sum of experimental[13] Δ_fH° for all molecules. The scale was extended to charged substituents by adding the gas-phase enthalpies of protonation (or deprotonation)[15] of the two bases (acids) which appear in eqn. (3).

Δ_4H°, eqn. (4), was obtained in the same way.

Δ_5H°, eqn. (5), was obtained from enthalpies ΔH°_{298} calculated at an MP2 level. Some values were calculated also for the cations but not for anions.

Each scale has some merits. All defining reactions are isodesmic[12a] but none are homodesmotic[12b] since one bond C_{sp3}–X is replaced by one bond C_{sp2}–X. In our opinion, it is not possible to construct a homodesmotic reaction suitable for our purpose. The values Δ_3H° are available for many substituents but need not represent a pure resonance due to different polarizabilities of the CH_3 and C_6H_5 groups. In addition they have a variable and not reliably known experimental uncertainty. The Δ_4H° values would be more convenient with respect to the polarizability but the values are available only for a limited number of substituents. The experimental uncertainty is certainly not smaller, probably somewhat greater than for Δ_3H°. The Δ_5H° scale was mainly based on calculation, *viz.* on the values of ΔH°_{298}(MP2). This scale seems to be theoretically reasonably based: the same system was advanced for estimating the constants $\sigma_R{}^\circ$ but instead of the energy the charge transfer was calculated.[11] In several cases, the calculated Δ_5H° values could be compared with experimental values (Table 1). The comparison seems not very satisfactory but it shows firstly the small dependability of experimental data. For instance, the experimental value for the substituents isopropyl and *tert*-butyl are certainly inaccurate: the calculated values are in better accord with the values for other alkyls. Note that some experimental values are based on measurements of unstable compounds like acrylic acid, styrene *etc.* In our opinion, the scale of calculated Δ_5H° values is consistent and should not be combined with experimental values. We considered also the possibility that our theoretical model was not sufficient for our purpose. We chose the substituent CF_3 for which the deviation from the expected values was the largest, and calculated the energies of the four compounds involved in eqn. (5) (C_2H_6, C_2H_4, $C_2H_5CF_3$ and $CH_2{=}CHCF_3$) using a DFT model B3LYP/6-311+G(3df,2pd)//MP2/6-31G(d,p). The results were not significantly different from the MP2 calculations (Table 1, footnote *h*). Therefore, we saw no reason to repeat all calculations with a more sophisticated model.

Our main task was to compare the new scales with each other and with the common scales σ_R. Comparison is not quite straightforward. Overall correlations were usually bad and it was necessary to take into account the different character of substituents. Let us compare first the new scales Δ_3H° and Δ_4H° derived in a very similar way. Correlation is bad (Table 2, line 1). A closer examination of a graph (not shown) reveals that the correlation depends strongly on the distant points (charged substituent O^-) and particularly the subgroup of donors shows no correlation at all. All Δ_4H° for donors are less negative than they should be, some are even positive. A formal explanation can be only a specific stabilizing interaction in *tert*-butyl derivatives, of an intensity comparable to the resonance in phenyl derivatives. This was already revealed from an analysis of Δ_fH° of various alkyl derivatives, and called φ-interaction.[19] No explanation is known. For the time being, we can only reject the

Table 1 Resonance effects of substituents calculated from the isodesmic reactions (kJ mol^{-1}, 298 K)

	Eqn. (3)		Eqn. (6)	Eqn. (4)	Eqn. (5)		
Substituent	$\Delta_3H°(g)$[a]	$\delta\Delta G°_{g\rightarrow w}$[b]	$\Delta_6G°(w)$	$\Delta_4H°(g)$[a]	$\Delta_5H°(g)$[c]	$\sigma_R°$[d]	$\sigma_R^{\pm}$[d]
H	0	0	0	0	0	0	0
CH_3	−23.2	0.6	−22.6	−1.3	−12.3 (−12.1)	−0.13	−0.32
C_2H_5	−23.6	0.4	−23.2	−10.3	−11.8 (−10.8)	−0.13	−0.30
$CH(CH_3)_2$	−18.8	0.9	−17.9	−8.7	−14.9 (−0.9)	−0.13[e]	−0.32
$C(CH_3)_3$	−15.6	−0.4	−16.0	−15.8	−15.0[f] (6.0)	−0.16	−0.17
$CH{=}CH_2$	−30.5	1.2	−29.3	−26.9	−28.6 (−26.1)	−0.01	−0.29
$C{\equiv}CH$	−15.6			4.5	−20.5 (3.0)	0.08	0.31[g]
C_6H_5	−25.6	4.5	−21.1	−11.3	−20.4 (−19.0)	−0.08	−0.30
CH_2OH	−23.0	5.2	−17.8	11.2	−4.7	−0.05	−0.07
CH_2SH	−18.5			5.6	−11.5	−0.07[e]	−0.10[e]
CH_2Cl	−26.2			−2.3	−6.4	−0.02	−0.14
CF_3	−11.9				6.1 5.0[h]	0.09	0.27
NH_2	−47.4			−9.9	−33.1	−0.48	−1.38
$N(CH_3)_2$	−80.7	10.9	−69.8		−33.6	−0.56	−1.85
OH	−52.8	5.6	−47.2	−1.4	−32.8	−0.43	−1.25
OCH_3	−40.8	15.5	−25.3	7.5	−17.6 (−8.4)	−0.43	−1.07
$OCOCH_3$	−27.1				1.5	−0.19	−0.61
SH	−19.0	6.4	−12.6	7.6	−13.8	−0.13	−0.33
SCH_3	−21.1	7.2	−13.9	2.3	−14.7	−0.15	−0.83
F	−19.0				−12.3 (−13.3)	−0.33	−0.52
Cl	−21.1	9.5	−11.6	20.2	−7.0 (−1.1)	−0.16	−0.31
Br	−16.0	9.2	−6.8	21.5	−0.3 (5.6)	−0.16	−0.30
I	−9.3	9.2	−0.1	18.8		−0.12	−0.28
CHO	−28.9	9.8	−19.1		−24.0 (−21.3)	0.23	0.70
$COCH_3$	−27.1	8.6	−18.5	−13.6	−19.9	0.16	0.51
COOH	−15.4			−16.3	−12.0 (−7.2)	0.16[e]	0.43
$COOCH_3$	−35.3	8.6	−26.7	−10.8	−13.6	0.16	0.41
CN	−12.6	10.6	−2.0	4.7	−11.4 (−8.2)	0.18	0.49
NO_2	−15.6	11.5	−4.1		−2.7	0.16	0.62
OH_2^+	−113.0			−12.3	21.8		
OH^+CH_3	−75.2			15.4	15.4		
$CH_2OH_2^+$	−25.0						
$CH{=}OH^+$	−85.8				(−39.3)		
$C(CH_3){=}OH^+$	−63.5						
$COOH_2^+$	−48.9						
$C(OCH_3){=}OH^+$	−60.0						
NH_3^+	−28.1			37.4	16.2[i]	−0.32	−1.48[g]
$NH^+(CH_3)_2$	−73.6		−32.7[j]		9.4		
$C{\equiv}NH^+$	−43.9				−4.5 (3.9)		
NO_2H^+	−75.0						
O^-	−184.1		−81.4[j]	−100.9		0.55	−2.04
CH_2^-	−191.4						
COO^-	−57.3					0.10	0.41[g]
CH_2O^-	−53.9			0.3			
$C{\equiv}C^-$	−59.1			−26.1			

[a] Derived from experimental $\Delta_fH°(g)$ from ref. 13, in the case of ionic substituents also from the gas-phase acidities or basicities from ref. 15. [b] Sum of $\Delta H°_{g\rightarrow w}$ from ref. 16. [c] Sum of $\Delta H°_{298}$ calculated at a MP2/6-31G(d,p) level, this work (in parentheses experimental values derived from $\Delta_fH°(g)$ from ref. 13). [d] Ref. 3. [e] Estimated. [f] Estimated from the calculations at the RHF level; at the MP2 level no convergence was achieved. [g] σ_R^- (acceptor substituents). [h] Obtained from the calculations at a B3LYP/6-311+G(3df,2pd)//MP2/6-31G(d,p) level, see Table SI, footnotes *a* and *b*. [i] Vinylamine is protonated preferentially on carbon, ref. 17, but our calculations relate to the protonation on nitrogen. [j] Calculated using also the dissociation constants in water, ref. 18.

values $\Delta_4H°$ for our present purpose. Comparison of $\Delta_3H°$ and $\Delta_5H°$ is not more favorable (Table 2, line 2) but reveals some specific features. Two substituents, CF_3 and $OCOCH_3$, give positive values $\Delta_5H°$: the ethene derivatives show an enhanced energy instead of lowered by resonance. We have no explanation for this fact. It is not dependent on the calculation of the enthalpies $\Delta H°_{298}$: if the calculations were based on the energies *E*(RHF), *E*(MP2) or *E*(B3LYP), the results were not significantly different. For the time being, we have excluded the two substituents from the correlations.

Therefore, we have focused our attention on $\Delta_3H°$, and its correlation with the standard scales of σ_R will be examined first. There is one important difference between these scales, the signs of σ_R have been chosen positive for the acceptors groups and negative for donors while all $\Delta_3H°$ are by definition negative. We accounted for this convention by assigning the $\Delta_3H°$ values positive or negative signs according to the sign of the pertinent σ_R. The resulting values are denoted $\pm\Delta_3H°$. In Figs. 1 and 2 they are correlated with two scales: $\sigma_R°$ and $\sigma_R^{\pm}$, respectively. (The latter symbol denotes σ_R^+ for donors and σ_R^- for acceptors, in both cases representing a strengthened conjugation.) The values of σ_R were taken from a standard recent collection.[3] Although they are of divergent precision and reliability, there is an advantage that all values could be taken from one source. The literature contains many collections of values (*e.g.*[2–4,6,11]) but many scales correlate closely.[11b] Figs. 1 and 2 reveal a significant feature of the correlations, *viz.* a systematic deviation of the CH_2X substituents in the sense of an increased stability of compounds $C_6H_5CH_2X$. To make this deviation more clear, we have included in Figs. 1 and 2 the substituents CH_2Br, CH_2I and $CH_2SO_2CH_3$ not included in Table 1; their values of $\Delta_3H°$ and the estimated σ_R^+ are less precise but the deviations are large and cannot be doubted. A possible explanation might be an interaction of the group X with π-electrons of the benzene ring (homoconjugation) which is not observed in solution in the model compounds used for defining σ_R. The

Table 2 Correlations of various scales of the resonance effect of dipolar substituents

	Explanatory variables	Response function	b^a		SD^b	R^b	N^b
1	$\Delta_3H°(\mathrm{g})$	$\Delta_4H°(\mathrm{g})$		0.46(9)	17.0	0.711	28^c
2	$\Delta_3H°(\mathrm{g})$	$\Delta_5H°(\mathrm{g})$		0.46(8)	6.3	0.756	26^d
3	$\sigma_\mathrm{R}{}^\circ$	$\pm\Delta_3H°(\mathrm{g})$		119(8)	8.8	0.928	25^e
4	$\sigma_\mathrm{R}{}^\pm$	$\pm\Delta_3H°(\mathrm{g})$		41.4(23)	7.8	0.966	25^e
5	$\sigma_\mathrm{R}{}^f$	$\pm\Delta_3H°(\mathrm{g})$		86(8)	11.2	0.918	25^e
6	σ_d	$\pm\Delta_3H°(\mathrm{g})$		88(8)	11.5	0.914	25^e
7	$\sigma_\mathrm{R}(\mathrm{g})^g$	$\pm\Delta_3H°(\mathrm{g})$		4.7(5)	9.2	0.950	13^e
8	σ_1, $\sigma_\mathrm{R}{}^\circ$	$\pm\Delta_3H°(\mathrm{g})$	4(5)	119(7)	8.7	0.952	25^e
9	$\lvert\sigma_\mathrm{R}{}^\pm\rvert$	$\Delta_3H°(\mathrm{g})$		35.0(35)	7.2	0.903	25
10	$\sigma_\mathrm{R}{}^\circ$	$\pm\Delta_5H°(\mathrm{g})$		66(6)	7.3	0.911	25^d
11	$\sigma_\mathrm{R}{}^\pm$	$\pm\Delta_5H°(\mathrm{g})$		23.2(21)	7.2	0.914	25^d
12	σ_I, $\sigma_\mathrm{R}{}^\circ$	$\pm\Delta_5H°(\mathrm{g})$	6(5)	68(6)	7.2	0.906	25^d
13	$\lvert\sigma_\mathrm{R}{}^\pm\rvert$	$\Delta_5H°(\mathrm{g})$		16.1(27)	6.0	0.776	25^d
14	$\sigma_\mathrm{R}{}^\pm$	$\Delta_6G°(\mathrm{w})$		31.3(34)	9.6	0.911	19^e
15	$\sigma_\mathrm{R}{}^\circ$	$\sigma_\mathrm{R}{}^\pm$		2.80(13)	0.16	0.965	29

[a] Slope with its standard deviation in parentheses. [b] Standard deviation from the regression, correlation coefficient and number of data, respectively. [c] Charged substituents included in this exceptional case. [d] Substituents CH=CH$_2$, CF$_3$ and OCOCH$_3$ eliminated. [e] Substituents CH$_2$X and CH=CH$_2$ eliminated. [f] Constants derived to be used for the gas-phase reactivities, ref. 4. [g] Constants derived here from the gas-phase reactions, see Discussion.

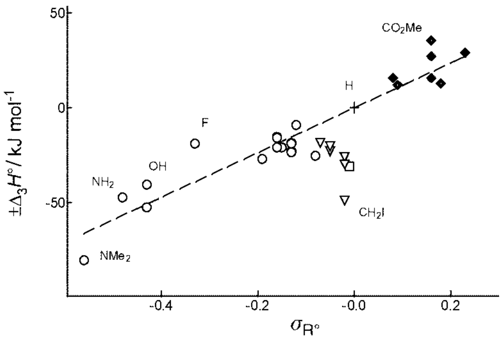

Fig. 1 Plot of the supposed resonance energies $\Delta_3H°$, eqn. (3), in benzene derivatives (taken as positive for acceptors, negative for donors) *vs.* the standard resonance constants $\sigma_\mathrm{R}{}^\circ$: ○ donors, ◆ acceptors, ▽ CH$_2$X groups, □ CH=CH$_2$, + hydrogen. The regression line relates to the combined set of donors, acceptors and hydrogen.

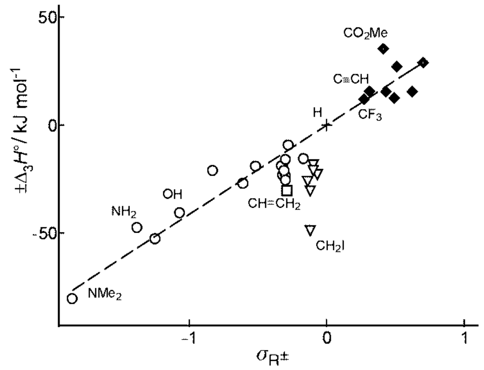

Fig. 2 Similar plot as in Fig. 1 using exalted resonance constants $\sigma_\mathrm{R}{}^+$ or $\sigma_\mathrm{R}{}^-$.

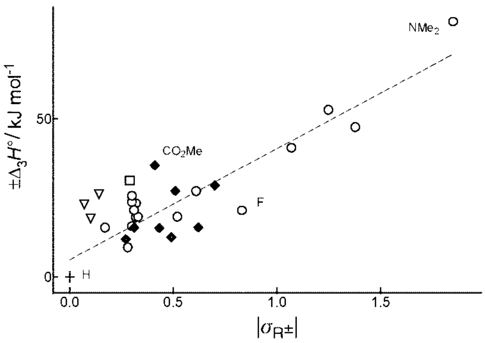

Fig. 3 Plot of the resonance energies $\Delta_3H°$, eqn. (3), *vs.* the absolute values of resonance constants $\sigma_\mathrm{R}{}^+$ or $\sigma_\mathrm{R}{}^-$, points denoted as in Fig. 1.

lowest-energy conformation of benzyl chloride, with the chlorine atom near to the benzene π-electrons,[20] is favorable for such interaction. Also an anomalous behavior of the substituent CH$_2$I observed in the electronic spectra[21] is in accord with this observation. Another irregularity in Figs. 1 and 2 is the deviation of the vinyl substituent: its $\Delta_3H°$ reveals a much stronger conjugation than anticipated from its σ_R. After excluding the substituents CH$_2$X and CH=CH$_2$, we obtained reasonably good correlations (Table 2, lines 3 and 4). There is an insignificant difference in using $\sigma_\mathrm{R}{}^\circ$ or $\sigma_\mathrm{R}{}^\pm$ since the two sets are themselves rather closely correlated (Table 2, line 15). Using other possible sets of constants does not improve the correlations (lines 5 and 6). In particular the constants σ_R recommended specially for gas-phase reactions[4] do not improve the correlation (line 5). We attempted to derive specific σ_R constants immediately from the acidobasic equilibria in the gas phase,[4] *viz.* from the difference between benzene *para* and *meta* derivatives. Correlation is not better (Table 2, line 7) and its value is impaired by the small number of available data.

Possible dependence of $\Delta_3H°$ on polarizability of the phenyl group was examined in two ways. Firstly, the polarization should be proportional to the polar character of the substituent as expressed by its inductive constant σ_I. A multiple regression with σ_I and σ_R as explanatory variables should improve the correlation—this is also standard procedure, common in DSP treatment of any data set.[2,4,6] The expectation has not been confirmed. Correlation in Table 2, line 8 is not better than in line 3, in particular the regression coefficient *b* at σ_I is not different from zero. The second test is based on the assumption that polarizability will increase the absolute value of $\Delta_3H°$ of all substituents. In a plot of $\pm\Delta_3H°$ *vs.* the absolute value of σ_R, the point for hydrogen should deviate downwards. This is apparently confirmed in Fig. 3 but with little significance: the intercept is 5.5 ± 2.4 kJ mol^{-1}. Correlation in Table 2, line 9 is somewhat worse than in line 4 due to the restricted range of values. We conclude that $\Delta_3H°$ express essentially the resonance, are not contaminated by inductive effect and only slightly by polarizability. For the latter, a correction of +5 kJ mol^{-1} could possibly be introduced but it is near to the possible experimental uncertainty.

The most characteristic feature of all resonance scales must be noted. In Figs. 1–3, the correlations are determined by donor substituents while the acceptors form merely a cluster of near points. This feature is caused by the different character of donor and acceptor substituents:[22] "Nature has endowed us

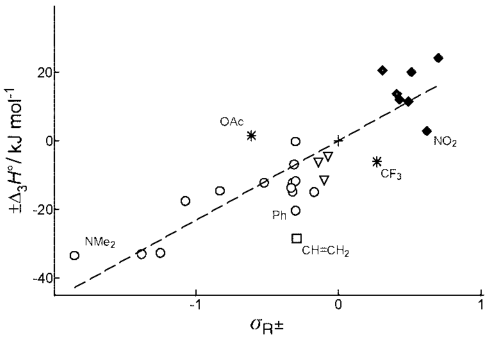

Fig. 4 Plot of the resonance energies Δ_5H°, eqn. (5), in ethene derivatives *vs.* the resonance constants $\sigma_R{}^+$ or $\sigma_R{}^-$, points denoted as in Fig. 1, $*$ points omitted in the correlation.

with a variation of donors while the common acceptors form a less diversified group."[22a] It has been postulated that uniform and relatively small values of σ_R of some important acceptors (particularly of NO_2, CN and CF_3, not of COX substituents) are not due to resonance and their σ_R should be equal to zero.[7] This is certainly true for reactions of many types[4,7] and could apply approximately even for Δ_3H° if a contribution of polarization were accounted for. Any scale of resonance effects is thus based mainly on strong donor groups: NH_2, NMe_2, OH, OR.

Resonance energies Δ_5H° were subjected to the same correlations with similar results as with Δ_3H° but always with a somewhat worse fit (Table 2, lines 10–12) even when the deviating substituents CF_3, OAc and vinyl were eliminated. Characteristic differences between acceptor and donors are observed even here (Fig. 4).

Resonance energies in solution

Energy quantities discussed hitherto, Δ_3H° and Δ_5H°, concerned isolated molecules, while the common constants σ_R have been derived mostly in aqueous solvents. The solvent effect may be estimated by deriving comparable quantities in water. We assume[23] that the reaction Gibbs energy of eqn. (3), Δ_3G°, equals its enthalpy Δ_3H°; this approximation is reasonable for isodesmic reactions of this type.[12c] Eqn. (3) can be now transferred into water by adding the solvation Gibbs energies $\Delta G^\circ_{g\rightarrow w}$ for all compounds involved. Relative values $\delta\Delta G^\circ_{g\rightarrow w}$ were derived from the experimental data[16] and are given in Table 1, column 3. (Theoretical calculation of $\Delta G^\circ_{g\rightarrow w}$ was not attempted.) This gives eqn. (6).

$$CH_3X(w) + C_6H_6(w) \rightleftharpoons XC_6H_5(w) + CH_4(w) \quad (6)$$

The reaction Gibbs energies $\Delta_6G^\circ(w)$, Table 1, column 4, are little different to Δ_3H°: solvation has only a minor effect on resonance. This is seen from the plot of $\Delta_6G(w)$ *versus* $\sigma_R{}^\pm$, Fig. 5, which is not much different from Fig. 2. Attenuation in solution is seen particularly in the smaller slope (Table 2, line 14 as compared to line 4), correlation is not improved but is somewhat worse. Differences between the scales Δ_3H° and $\sigma_R{}^\pm$ cannot be thus attributed simply to solvation. One would expect that specific substituent effects of the CH_2X will be attenuated in solution: it is probable but not proven by Fig. 5 since $\Delta_6G^\circ(w)$ is available only for the substituent CH_2OH.

Preceding analysis of resonance effects in terms of substituent constants[8] gave somewhat different results, particularly that the resonance effect of common substituents is strengthened in water (Specific Substituent Solvation Assisted Resonance). In Table 1, we find no substituent for which $\Delta_3G^\circ(w)$ would be greater in absolute value than Δ_3H°. Resonance is attenuated in water in all cases but when it is related to the inductive effect, it may appear as relatively strengthened since the inductive effect

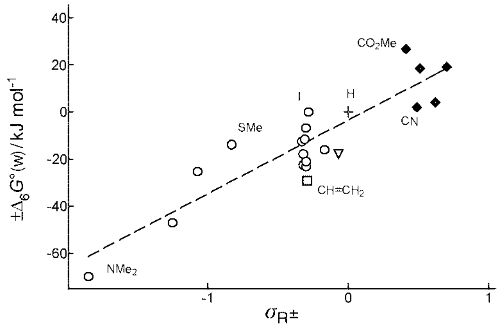

Fig. 5 Plot of the resonance energies in water Δ_6G°, eqn. (6), (positive for acceptors, negative for donors) *vs.* the resonance constants $\sigma_R{}^+$ or $\sigma_R{}^-$.

is attenuated more.[23] This can be anticipated from the much greater charge delocalization in the ions with resonance than those with an inductive effect.

Charged substituents

Substituent groups with a positive or negative charge (Table 1, lower part) were excluded from all correlations, partly because no reliable values of σ_R were available for comparison. A few values reported[3,6] are strongly dependent on solvent, ionic strength or on the model used, and cannot be used for this purpose. Values of Δ_3H° in the lower part of Table 1 thus represent the first reliable estimates for charged groups. Some values are readily understandable: particularly the great negative values for the negatively charged substituents O^-, $CH_2{}^-$ and positively charged COH^+X can be visualized by plausible resonance formulas. On the other hand, certain other values can be hardly understood in terms of resonance, as the appreciable value for $NH_3{}^+$ and particularly the large negative value for $OH_2{}^+$. It seems that the polarizability effects, negligible for neutral substituents, are very important for charged substituents. An interesting substituent is NO_2H^+, isoelectronic with COOH, which can be investigated only in the gas phase: its strong resonance can be hardly pictured by a reasonable resonance formula.[24]

Conclusions

Differences between the individual scales of resonance are certainly due partly to the unknown experimental errors in Δ_3H° and unknown reliability of calculations of Δ_5H°; partly they are due to specific features observed only in the gas phase (CH_2X substituents). However, there still remain differences exceeding possible errors and exceeding also the solvent effect (compare Δ_3H° and Δ_6G°). In our opinion, an explanation can be sought only in the influence of charge. While Δ_3H° and Δ_5H° were determined here on neutral monofunctional molecules, the scales of σ_R have been defined on bifunctional derivatives, either on the basis of ionization processes (benzoate anions, phenolate anions, anilinium cations) or of strongly polar transition states (solvolysis of cumyl chlorides). Resonance of some groups may be different in these two cases. In this respect, the quantum chemical procedure based on charges[11] appears a better approximation of the practical scale σ_R than a procedure based on energies which has been used in this paper.

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