Stabilization of Charged Substrates by First- and Second-Row Heteroatoms

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Abstract: Ab initio MO calculations of model systems and the linear combination of fragment configurations (LCFC) method are used to determine the relative ability of first- and second-row heteroatoms to stabilize charged substrates via a σ effect. It is predicted that second-row heteroatoms will stabilize both cationic and anionic substrates more than their first-row counterparts when the charge on the substrate is localized. If the charge is delocalized, a first-row heteroatom will stabilize either the cationic or the anionic substrates more than a corresponding second-row heteroatom. Furthermore, it is predicted that a second-row heteroatom will always absorb more of the excess charge from the charged substrate than its first-row counterpoart, regardless of whether the charge is delocalized or not. It is concluded that there is not necessarily a relationship between the ability of a substituent to withdraw or release electrons and its ability to stabilize anionic or cationic substrates. A compilation of experimental data is presented in support of the theoretical analysis.

Introduction

The assumption that a negatively charged substrate will prefer an electronegative substituent because of its ability to withdraw electrons and that a positively charged substrate will prefer an electropositive substituent because of its ability to donate electrons is a popular idea[1] that is not supported by a large volume of evidence.[2] Indeed, examples of the reverse trend have appeared in the literature,[3] e.g., the central carbon atom of a tertiary carbonium ion has been found to be more positively charged than the corresponding carbon in the less stable secondary species.[3a]

The difference in the ability of first- and second-row heteroatoms of the same column of the periodic table to stabilize charged substrates is a clear example of the inadequacies of classical inductive effects. By adhering to the classical analysis, one expects the more electronegative first-row heteroatoms to stabilize an anionic moiety more than their second-row counterparts. The reverse is expected if a cationic substrate is involved. These predictions are in contrast to the evidence gathered from numerous experimental and computational investigations.[4-11] Chlorine and sulfur have been shown to stabilize adjacent anionic centers more than fluorine or oxygen, respectively.[4] On the other hand, carbon, oxygen, and fluorine have been found to stabilize solvated cationic substrates better than their second-row counterparts.[5] This latter trend reverses in the gas phase.[6]

A variety of π effects have been proposed to explain these observations. These include the following.

(A) The greater stabilization of anionic substrates by second-row substituents has been postulated to be due to the low-lying d orbitals present in the second-row elements but absent in the first-row heteroatoms.[4k] However, d orbitals in divalent sulfur have been shown to have no significant effect on the stabilization of an adjacent carbanion.[4h,7]

(B) It has been argued that carbanions are destabilized less by lone pair–lone pair repulsion when substituted by chlorine or sulfur in comparison to fluorine or oxygen.[1a,5b,8] However, if lone pair–lone pair repulsion is more important than inductive effects, why do chlorine and sulfur stabilize adjacent carbanions more than methyl or hydrogen?[4a,b,d]

(C) It was proposed that $>CH_2SR^{1-}$ is more stable than $>CH_2OR^{1-}$ because of a hyperconjugative interaction between the lone pair on carbon and the low-lying σ^*_{SR} orbital.[9,10] Although this accounts for the preferred conformation of these anions, it cannot be the entire explanation as no such interactions are possible in $>CH_2Cl^{1-}$ and $>CH_2F^{1-}$.

(D) The assumption that 2p–2p π overlap is superior to 3p–2p π overlap initiated the proposal that the positive charge on carbonium ions bearing first-row substituents is more delocalized than the charge on carbonium ions bearing second-row substituents. However, several theoretical investigations have shown that the

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Table I. Total Energies[a] of H*X (X = F, Cl, OH, SH) and Gross Charges[b] on X Computed with the STO-3G Basis

Z_{H^*}	X	total energy	gross charge on X
0.70	F	−98.2842	−0.37
0.85	F	−98.4238	−0.29
1.00	F	−98.5711	−0.21
1.15	F	−98.7263	−0.12
1.30	F	−98.8898	−0.04
1.45	F	−99.0619	+0.05
0.70	Cl	−454.8859	−0.46
0.85	Cl	−455.0022	−0.32
1.00	Cl	−455.1344	−0.17
1.15	Cl	−455.2841	−0.01
1.30	Cl	−455.4520	+0.15
1.47	Cl	−455.6387	+0.31
0.55	OH	−74.5232	−0.49
0.70	OH	−74.6551	−0.40
0.85	OH	−74.7969	−0.30
1.00	OH	−74.9491	−0.20
1.15	OH	−75.1123	−0.09
1.30	OH	−75.2868	+0.01
1.45	OH	−75.4728	+0.11
0.55	SH	−393.8667	−0.46
0.70	SH	−393.9869	−0.31
0.85	SH	−394.1243	−0.16
1.00	SH	−394.2805	+0.01
1.15	SH	−394.4565	+0.17
1.30	SH	−394.6528	+0.34
1.45	SH	−394.8690	+0.49

[a] Standard bonds lengths and bonds angles were used.[16]
[b] Charges were calculated via the Mulliken approximation: R. S. Mulliken, *J. Chem. Phys.*, 1833, 1841, 2338, 2343 (1955).

opposite is true[11a–c] and ^{13}C NMR results suggest that the carbonium ion is more positively charged when bound to a first-row heteroatom than to a second-row heteroatom.[11d] Furthermore, this explanation does not rationalize the difference in the solution and gas-phase trends.

Here we report the following.

(1) Ab initio MO calculations of model systems suggest that it is not necessary to invoke π effects to explain the greater stabilization of charged substrates by second-row heteroatoms relative to their first-row counterparts. Situations are predicted to occur where first-row heteroatoms will stabilize charged substrates more than the corresponding second-row heteratoms.

(2) The linear combination of fragment configurations, LCFC,[12] method is used to view the problem from a qualitative standpoint. A qualitative model is proposed that easily rationalizes the quantitative results.

(3) Both the qualitative and quantitative methods suggest that there is no relationship between the ability of a substituent to stabilize a charged substrate and its ability to absorb excess charge from it.

Computational Method

In order to compare the stabilization of a charged substrate by first- and second-row heteroatoms in the absence of π effects, we performed the following computational experiment. Reactions 1 and 2 were studied with ab initio MO calculations using the

$$H^*{-}F + H{-}Cl \rightarrow H^*{-}Cl + H{-}F \qquad (1)$$

$$H^*{-}OH + H{-}SH \rightarrow H^*{-}SH + H{-}OH \qquad (2)$$

STO-3G[13] basis set. Rection 1 was also studied with the 4-31G[14] basis set. The nuclear charge on H*, Z_{H^*}, was varied so that it serves as a model for a charged substrate. A nuclear charge greater than 1.0 mimics a positively charged substrate while a nuclear charge less than 1.0 mimics a negatively charged substrate.

Table II. Total Energies[a] of H*X (X = F, Cl) and Gross Charges[b] on X Computed with the 4-31G Basis

Z_{H^*}	X	total energy	gross charge on X
0.70	F	−99.6506	−0.655
0.85	F	−99.7616	−0.575
0.90	F	−99.8017	−0.545
0.95	F	−99.8436	−0.513
1.00	F	−99.8872	−0.479
1.15	F	−100.0303	−0.366
1.30	F	−100.1938	−0.238
1.45	F	−100.3805	−0.096
0.70	Cl	−459.3353	−0.482
0.85	Cl	−459.4383	−0.362
0.90	Cl	−459.4771	−0.319
0.95	Cl	−459.5185	−0.275
1.00	Cl	−459.5625	−0.229
1.15	Cl	−459.7123	−0.083
1.30	Cl	−459.8917	+0.070
1.45	Cl	−460.1040	+0.224

[a] Standard bond lengths and bond angles were used.[16]
[b] Charges were calculated via the Mulliken approximation: R. S. Mulliken, *J. Chem. Phys.*, 1833, 1841, 2338, 2343 (1955).

Table III. Energetics and Charge Flow of Reaction 1[a]

nuclear charge on H*	r_{H^*-F},[b] Å	r_{H^*-Cl}, Å	ΔH, kcal	Δq[c]
0.7	0.995	1.357	−32	+0.07
1.0	0.955	1.313	0	0.00
1.3	0.937	1.287	+19	−0.09

[a] Computed at the STO-3G level. [b] Optimized bond length. [c] $\Delta q = q_F(H^*{-}F) + q_{Cl}(H{-}Cl) - q_F(H{-}F) - q_{Cl}(H^*{-}Cl)$, where q_X is the gross atomic charge on X.

The total energies and charge densities, q, of the molecules studied are presented in Tables I and II. Plots of ΔH and Δq (eq 3) vs. the initial charge on H*, $Z_{H^*} - 1.0$, are shown in Figures

$$\Delta q = q_X(H^*{-}X) + q_{X'}(H{-}X') - q_{X'}(H^*{-}X') - q_X(H{-}X) \qquad (3)$$

$$X = F, OH;\ X' = Cl, SH$$

1 and 2. When ΔH is negative, the charged substrate prefers the second-row substituent. When Δq is negative, more positive charge (or less negative charge) is absorbed from the charged substrate by the second-row heteroatom than by its first-row counterpart. When Δq is positive, the opposite is true.

Results and Discussion

(A) **Computational Results.** Examination of Figures 1 and 2 reveals the following trends.

(1) Reactions 1 and 2 are found to be exothermic when the initial charge on H* is either very negative or very positive; i.e., when the absolute magnitude of the initial charge on the substrate is very large, it is stabilized more by a second-row substituent than by the corresponding first-row substituent. These results suggest that it is not necessary to invoke π effects to explain the greater stabilization of charged substrates by second-row heteroatoms relative to their first-row counterparts.

(2) As the initial charge on H* increases from a negative to a positive value, Δq is found to decrease from a positive to a negative value; i.e., the second-row substituent always absorbs more of the excess charge from the charged substrate than the corresponding first-row heteroatom.

(3) In Figure 1 the maximum of the curve occurs when the initial charge on H* is small and corresponds to a positive value of ΔH. This suggests that when the initial charge on a substrate is small, first-row substituents will stabilize either a positively or negatively charged substrate more than second-row substituents.

(4) A comparison of points 2 and 3 results in the conclusion that there will be a point where a first-row substituent will stabilize a charged substrate more than its second-row counterpart even though the latter substituent will absorb more of the excess charge than the former substituent. The results presented in Table III

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(12) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974); N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1924, 1935, 1941 (1972).

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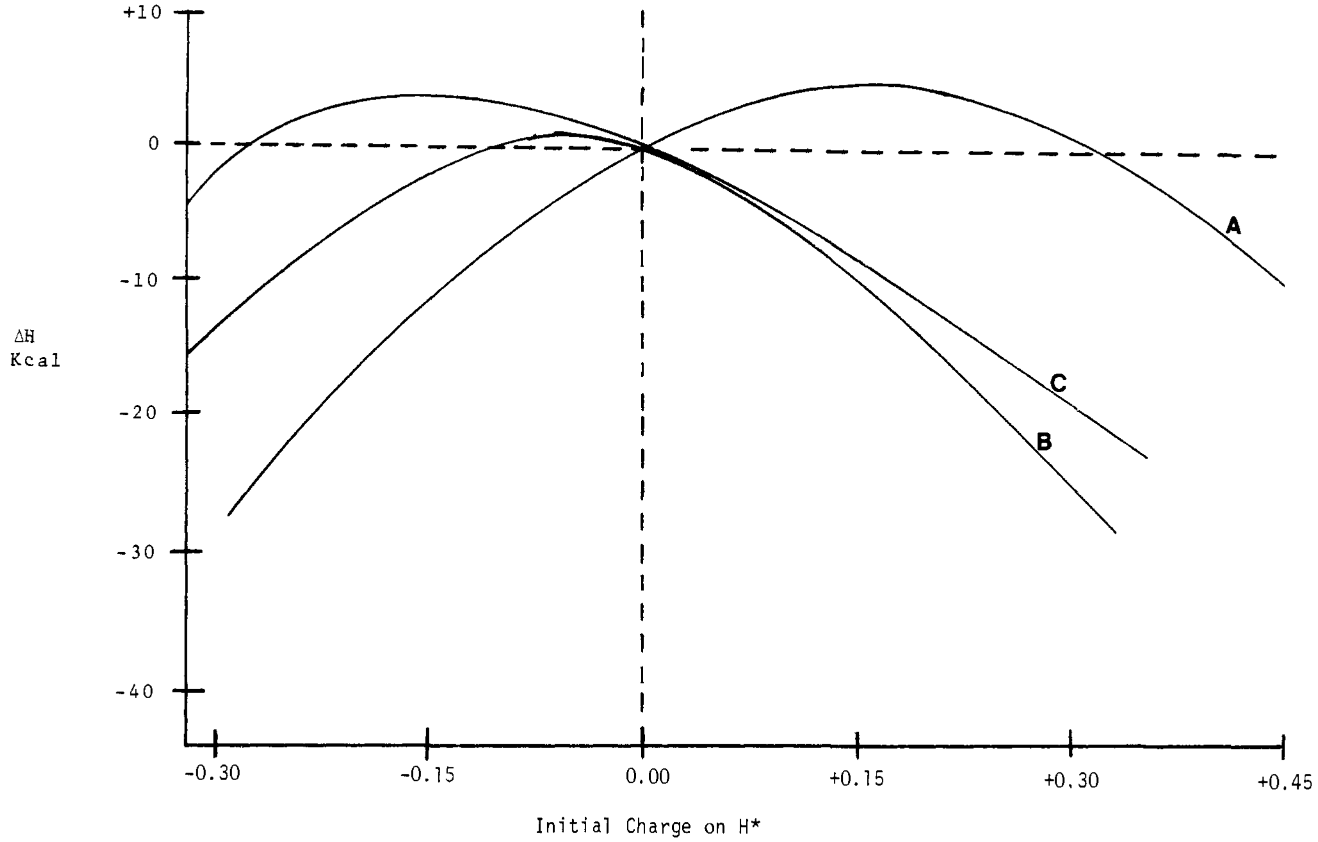


Figure 1. (A) Computed (STO-3G basis set) variation of ΔH for reaction 1 vs. the intial charge on H* ($Z_{H^*} - 1.0$). (B) Computed (STO-3G basis set) variation of ΔH for reaction 2 vs. the intial charge on H* ($Z_{H^*} - 1.0$). (C) Computed (4-31G basis set) variation of ΔH for reaction 1 vs. the initial charge on H* ($Z_{H^*} - 1.0$).

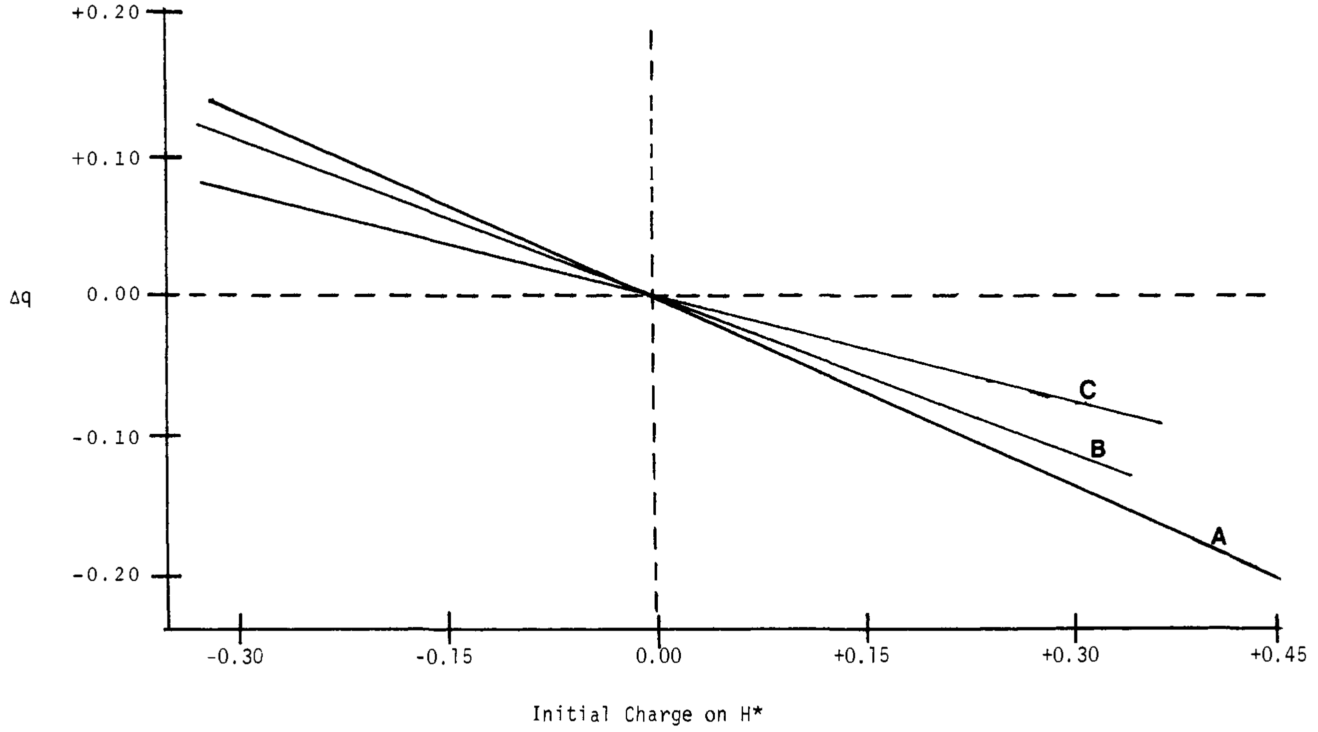
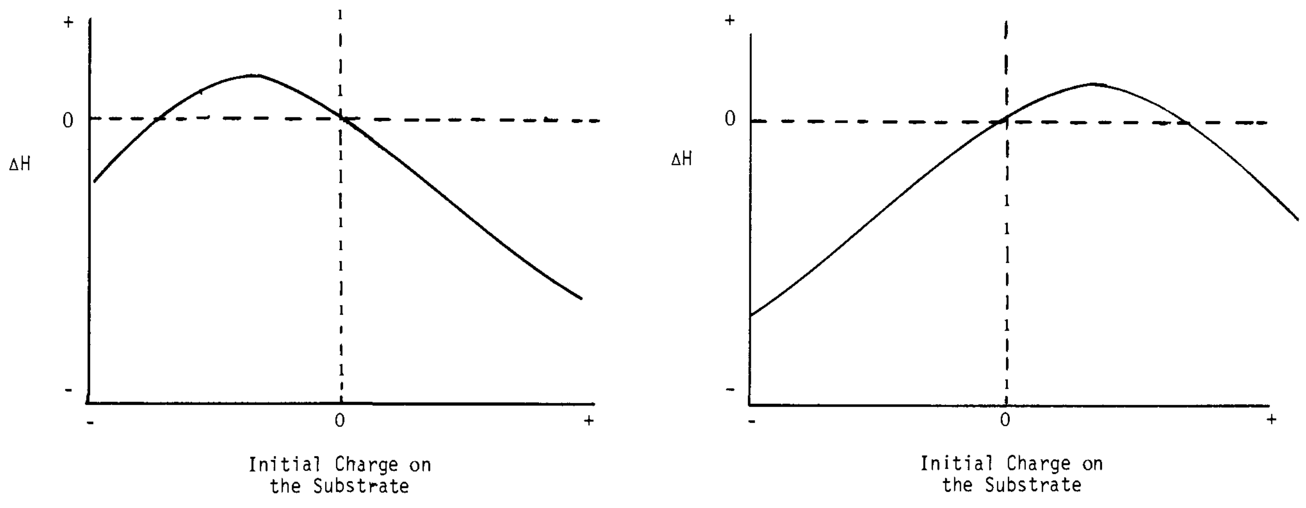


Figure 2. (A) Computed (STO-3G basis set) variation of Δq for reaction 1 vs. the intial charge on H* ($Z_{H^*} - 1.0$). Δq is defined in eq 3. (B) Computed (STO-3G basis set) variation of Δq for reaction 2 vs. the initial charge on H* ($Z_{H^*} - 1.0$). Δq is defined in eq 3. (C) Computed (4-31G basis set) variation in Δq for reaction 1 vs. the initial charge on H* ($Z_{H^*} - 1.0$). Δq is defined in eq 3.

show that this expectation is not altered by the optimization of the H*–Cl and H*–F bond lengths. Therefore, the computational results presented here suggest that the ability of a substituent to stabilize a charged substrate can be independent of its ability to absorb excess charge from the charged substrate.

The basis set dependence of Figure 1 deserves comment. The STO-3G basis (Figure 1A) predicts that fluorine will stabilize a positively charged substrate relative to chlorine while the 4-31G basis (Figure 1C) predicts that a negatively charged substrate will prefer fluorine over chlorine. It is easily shown that these results

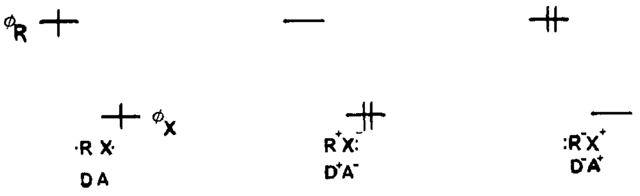
Scheme I



Z_{H^*}=1.0 used as the neutral substrate

Z_{H^*}=0.85 used as the neutral substrate

Scheme II



are dependent on the choice of the neutral substrate. The charge on the carbon possesing the unpaired electron in the following substrate radicals probably is never zero. Therefore, the choice

$$H_3C\cdot \qquad F_3C\cdot \qquad (CH_3)_3C\cdot \qquad C_6H_6CH_2$$

of Z_{H^*} = 1.0 for the neutral substrate is arbitrary. If the atom of the neutral substrate radical that will be bound to the substituent has a negative charge, then Z_{H^*} = 0.85 would be an appropriate choice to mimick the neutral substrate. If the 4-31G results are replotted by using Z_{H^*} = 0.85 for the neutral substrate, the resulting curve resembles that of Figure 1A. This is depicted in Scheme I. Therefore, it is clear that the nature of the substrate plays a large role in determining if fluorine will stabilize a positive or a negative charge on a substrate relative to chlorine.

In order to take these quantitative calculations seriously, one must be able to understand them on a qualitative level and see how they match up with the known experimental data. In the following two sections a qualitative explation of the ab initio results and a compilation of experimental results are presented.

(B) The LCFC Approach to Substituent Effects. The approach employed here is based on the linear combination of fragment configuratins (LCFC) method at the level of zero interfragmental overlap.[12] The molecule R–X, where R is the substrate and X is the substituent, will be used to illustrate the theoretical analysis.

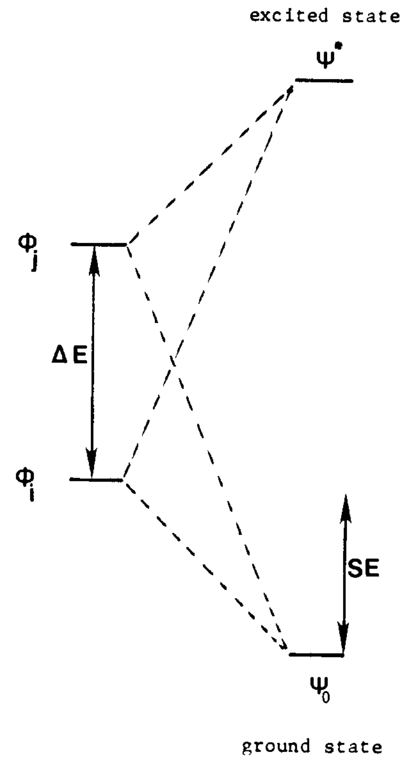
(1) The Ground State of R–X. The basis set configurations, which contain only the singly occupied orbitals, ϕ_R and ϕ_X of the radical fragments, R· and X·, are shown in Scheme II. The relative energies of no bond, DA, and two charge-transfer configurations, D^+A^- and D^-A^+, are calculated empirically with eq 4–6, where the symbols *I*, *A*, and *C* represent the ionization potential and the electron affinity of the radical fragment and the coulomb attraction between the two charged fragments in the ionic configurations, respectively.

$$E_{DA} = 0 \tag{4}$$

$$E_{D^+A^-} = I(R\cdot) - A(X\cdot) + C \tag{5}$$

$$E_{D^-A^+} = I(X\cdot) - A(R\cdot) + C \tag{6}$$

Scheme III



The energy of the ground state of R–X, Ψ_0, is determined by the interaction of the DA configuration with the D^+A^- and D^-A^+ configurations. In general, the stabilization (SE) caused by the interaction of any two configurations ϕ_i and ϕ_j (see Scheme III) is given by eq 7.[15] The wave function for the resulting ground

$$SE = -\beta - \Delta E/2 - \Delta E^2/8\beta \tag{7}$$

state, Ψ_0, is given by eq 8. The mixing coefficient, λ, is given in eq 9.[15] In eq 7 and 9, ΔE and β are the energy gap separating

$$\Psi_0 = (1/(1 + \lambda^2)^{1/2})(\phi_i + \lambda\phi_j) \tag{8}$$

$$\lambda = 1 + \Delta E/2\beta + \Delta E^2/8\beta^2 \tag{9}$$

ϕ_i and ϕ_j and their interaction matrix element. In the case of the interaction of the DA with either the D^+A^- or the D^-A^+, β is

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[15] Equations 7 and 9 arise from the solution of a 2 × 2 secular determinant where it is assumed that $4\beta^2 \gg \Delta E^2$. This is a good approximation for a σ bond at the equilibrium bond length.

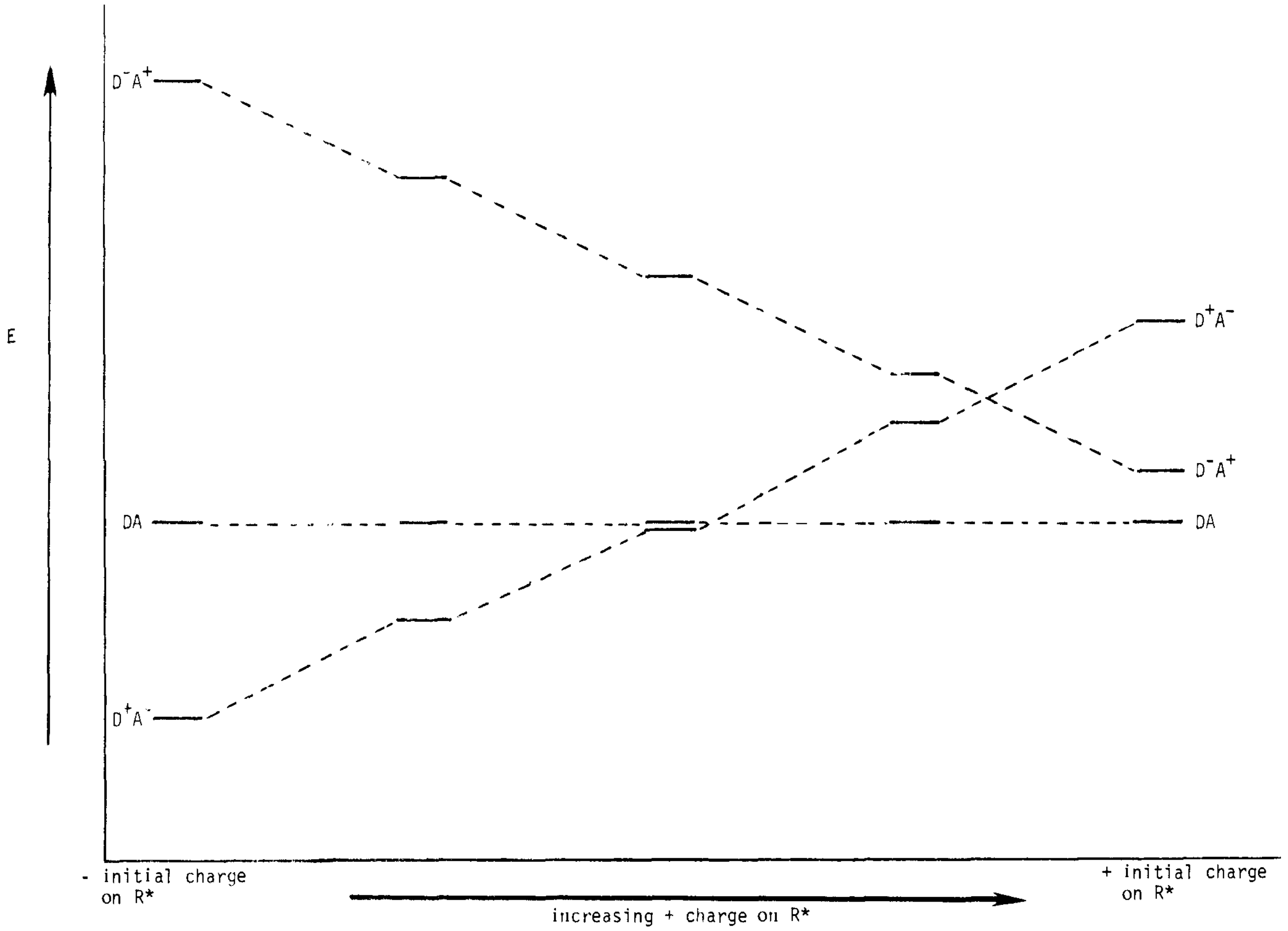

Figure 3. The change in the energies of the D$^+$A$^-$ and D$^-$A$^+$ configurations relative to the DA configuration of R*–X as a function of the initial charge on R*.

proportional to the overlap of the two orbitals ϕ_R and ϕ_X, S. In eq 10 K is an energy constant that increases as the electronegativities of R and X increase. By definition ΔE, SE, and λ are positive quantities and β is a negative quantity. SE and λ will increase in magnitude as $|\beta|$ increases and ΔE decreases.

$$\beta = \langle DA|H|D^+A^-\rangle = \langle DA|H|D^-A^+\rangle = KS \qquad (10)$$

The magnitude of SE determines the energy of the ground state of the species found in (11); therefore, it also determines ΔH for this reaction. The magnitude of λ determines the contributions that the DA, D$^+$A$^-$, and D$^-$A$^+$ configurations make to the ground state: therefore, λ determines Δq for reaction 11.

$$R^*\text{–}X + R\text{–}X' \rightarrow R^*\text{–}X' + R\text{–}X \qquad (11)$$

$$X = F, OH;\ X' = Cl, SH$$

In a comparison of R–F and R–Cl one must consider the following.

(a) $|\beta(RF)| > |\beta(RCl)|$ since F is more electronegative than Cl. If one uses the CNDO[16] paramiterization $\beta(CH_3F) = -14$ eV and $\beta(CH_3Cl) = -11$ eV.

(b) The energy gap separating the DA and the D$^+$A$^-$ configurations, ΔE(DA–D$^+$A$^-$), for R–F is about equal to that for R–Cl. This is because the electron affinity for F (3.4 eV) is about equal to that of Cl (3.6 eV).

(c) The ΔE(DA–D$^-$A$^+$) for R–F is much greater than that for R–Cl, as the ionization potential of F (17.4 eV) is much greater than that of Cl (13.0 eV).

Similar trends are found for comparisons of SH and OH, CH$_3$ and SiH$_3$, etc.

Our purpose now is to understand how ΔH and Δq for reaction 11 will vary vs. the initial charge on the charged substrate.

(2) The Transformation of R into a Charged Substrate. The loss of an anionic leaving group from R or the addition of a proton to R will cause R to have an initial positive charge. The D$^+$A$^-$ is destabilized and the D$^-$A$^+$ is stabilized relative to the DA by this transformation (Figure 3). The reverse will occur if R loses a proton and becomes negatively charged (Figure 3). In other words, ΔE(D$^+$A$^-$) and ΔE(D$^-$A$^+$) increase or decrease as the initial charge on R* is altered. In order to determine how the transformation of R to a charged substrate will effect ΔH and Δq for reaction 11, we must determine the change in SE and λ with respect to a change in ΔE; i.e., eq 7 and 9 must be differentiated with respect to ΔE. This results in eq 12 and 13.

$$\frac{\delta SE}{\delta \Delta E} = -\tfrac{1}{2}\left(1 + \frac{\Delta E}{2\beta}\right) \qquad (12)$$

$$\frac{\delta \lambda}{\delta \Delta E} = \frac{1}{2\beta}\left(1 + \frac{\Delta E}{2\beta}\right) \qquad (13)$$

Examination of eq 12 and 13 results in the two following rules. Rule 1: the magnitude of a change in SE, induced by a perturbation in ΔE, will increase as the magnitude of β increases and as the magnitude of ΔE (in the unperturbed system) decreases. Rule 2: The magnitude of a change in λ, induced by a perturbation in ΔE, will increase as the magnitudes of β and ΔE (in the unperturbed system) decrease.

Rules 1 and 2 are illustrated by the computed values of SE and λ presented in Table IV. A comparison of entries a–c and d–f of Table IV reveals that both SE and λ decrease as ΔE increases. The rate of decrease in SE is greater when $\beta = -15.0$ eV than when $\beta = -10.0$ eV; in contrast the decrease in λ is faster when

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[16] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

Table IV. Computed Values of SE[a] and λ[b]

entry	β_{RX}	ΔE, eV	SE, eV	ΔSE, eV	λ	$\Delta\lambda$
a	−10.0	4.0	8.20	1.40	0.820	0.140
b	−10.0	8.0	6.80	1.00	0.680	0.100
c	−10.0	12.0	5.80		0.580	
d	−15.0	4.0	13.13	1.60	0.876	0.108
e	−15.0	8.0	11.53	1.33	0.768	0.088
f	−15.0	12.0	10.20		0.680	

[a] Equation 7. [b] Equation 9.

$\beta = -10.0$ eV as compared to $\beta = -15.0$ eV. A comparison of entries a and b vs. entries b and c reveals that both SE and λ change faster the smaller the magnitude of ΔE.

Rules 1 and 2 are used to predict trends in ΔH and Δq for reaction 11 as the initial charge on R* is changed from negative to positive.

(a) ΔH for Reaction 11. Examination of Figure 3 reveals that as the initial negative charge on R decreases ΔE(DA–D$^+$A$^-$) decreases. ΔE(DA–D$^-$A$^+$) also decreases, but this energy gap is so large that it is assumed that the contribution of the D$^-$A$^+$ configuration in the ground state can be neglected until R* is positively charged. The decrease in ΔE(DA–D$^+$A$^-$) causes an increase in SE which is expected to be larger for R*–F than for R*–Cl as β(RF) is greater than β(RCl). Therefore, as the negative charge on R* is initially decreased, ΔH for reaction 11 is expected to become increasingly positive.

As the initial negative charge on R* continues to decrease, the D$^+$A$^-$ will eventually cross the DA and ΔE(DA–D$^+$A$^-$) will increase. This will cause SE to decrease. The decrease in SE is expected to be greater for R*–F than for R*–Cl as β(RF) is greater than β(R–Cl). Therefore, as the positive charge on R* increases, ΔH for reaction 11 is expected to become more negative. The increase in the DA–D$^-$A$^+$ interaction, caused by the decrease in ΔE(DA–D$^-$A$^+$), is not expected to alter this prediction as the greater magnitude of β(RF) is cancelled out by the relatively smaller magnitude of ΔE(DA–D$^-$A$^+$) for R–Cl.

(b) Δq for Reaction 11. Examination of Figure 3 reveals that as the initial negative charge on R* decreases ΔE(DA–D$^+$A$^-$) decreases. Again the contribution of the D$^-$A$^+$ configuration is ignored until R* becomes positively charged. The decrease in ΔE(DA–D$^+$A$^-$) will cause increase in λ which in turn will cause an increase in the contribution of the DA configuration in the ground state. This will cause a decrease in the negative charge on X. This change will be faster for R–Cl than for R–F since β(RF) > β(RCl). Therefore, Δq is expected to decrease.

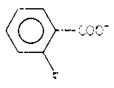
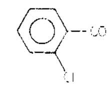
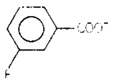
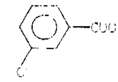
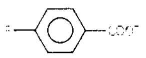
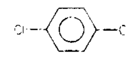
As the initial negative charge on R* continues to decrease, the D$^+$A$^-$ will cross the DA and ΔE(DA–D$^+$A$^-$) will increase. This will cause Δq to become more negative. A contributing factor in the decrease of Δq will be the decrease in ΔE(DA–D$^-$A$^+$) as this energy gap is smaller for R–Cl than for R–F. Therefore, Δq is expected to change continuously from a positive to a negative value as the initial charge on R* is changed from negative to positive.

(c) Conclusions from the LCFC Analysis. (i) Reaction 11 is expected to be exothermic when the initial charge on R* is either very negative or positive.[17a] This is found in the ab initio results (Figure 1). The LCFC analysis teaches that this behavior is due to the smaller β for R–Cl than for R–F. *This leads to the conclusion that second-row substituents stabilize anionic substrates more than their first-row counterparts because they are less electronegative.*

(ii) Δq for reaction 11 is expected to decrease continuously from a positive to a negative value as the initial charge on R* is changed from negative to positive. This is also found in the ab initio results (Figure 2). This phenomenon is again primarily due to the fact that β(RCl) < β(RF).

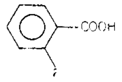
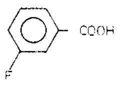
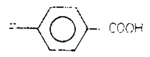
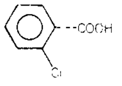
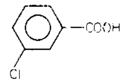
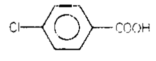
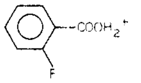
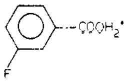
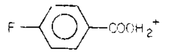
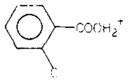
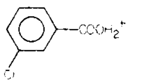
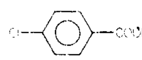
(iii) The position of the maximum for a plot of ΔH vs. the initial charge on R* cannot be determined qualitatively. The position

Table V. Proton Affinities for Benzoate Anions[a]

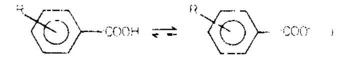
anion	PA, kcal	anion	PA, kcal
	335		333
	333		33?2
	334		332

[a] R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Am. Chem. Soc.*, 96, 4035 (1974).

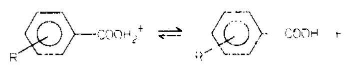
Table VI. pK_a Values for Substituted Benzoic Acids in Aqueous Solution at 25 °C

compd	pK_a	ref
	−3.27[c]	*a*
	3.86[c]	*a*
	4.14[c]	*a*
	2.92[c]	*a*
	3.82[c]	*a*
	3.98[c]	*a*
	−7.60[c]	*b*
	7.62[d]	*b*
	−7.30[d]	*b*
	−7.68[d]	*b*
	−7.73[d]	*b*
	−7.48[d]	*b*

[a] G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, 1961. [b] D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London, 1965. [c] pK_a for the equilibrium



[d] pK_a for the equilibrium



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(17) (a) This trend was noted by Schubert et al. over 20 years ago. See: W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962); W. M. Schubert, H. Steadly, and J. M. Craven, *J. Am. Chem. Soc.*, **82**, 1353 (1960); W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960); W. M. Schubert, J. M. Craven, and H. Steadly, *ibid.*, **81**, 2695 (1959); W. M. Schubert, J. M. Craven, H. Steadly, and J. Robins, *J. Org. Chem.*, **22**, 1287 (1957). (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1969. W. T. Borden, "Modern MO Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, N.J., 1975.

Table VII. The pK_a's of Some Substituted Anilines and Pyridines[a]

base	pK_a	base	pK_a
3-fluoroaniline	3.6	4-methylthioaniline	4.4
3-chloroaniline	3.5	3-fluoropyridine	3.0
4-fluoroaniline	4.7	3-chloropyridine	2.8
4-chloroaniline	4.2	3-methoxypyridine	4.9
3-methoxyaniline	4.2	3-methylthiopyridine	4.4
3-methylthioaniline	4.0	4-methoxypyridine	6.5
4-methoxyaniline	5.3	4-methylthiopyridine	5.9

[a] D. D. Perrin "Dissociation Constants of Organic Basis in Aqueous Solution", Butterworths, London, 1965.

Table VIII. Proton Affinities for Substituted Acetate Anions[a]

acid	PA, kcal	acid	PA, kcal
$CHF_2CO_2^-$	327	$CH_2FCO_2^-$	335
$CHCl_2CO_2^-$	326	$CH_2ClCO_2^-$	333

[a] K. Hirakoa, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, 95, 6833 (1973).

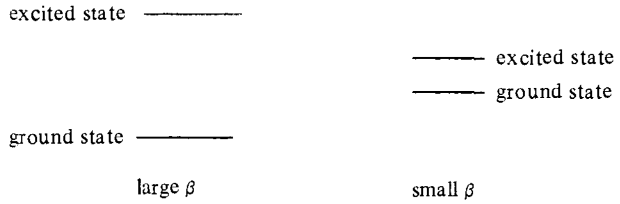
Table IX. pK_a Values for Substituted Acetic Acids in Aqueous Solution at 25 °C[a]

acid	pK_a	acid	pK_a
CH_2FCO_2H	2.7	CF_3CO_2H	0.2
CH_2ClCO_2H	2.9	CCl_3CO_2H	0.6

[a] G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants for Organic Acids in Aqueous Solution", Butterworths, London, 1961.

of the maximum is seen to depend on the difference in β(RF) and β(RCl), $\Delta E(DA\text{-}D^+A^-)$ and $\Delta E(DA\text{-}D^-A^+)$ for R–F and R–Cl. Therefore, it is clear that the position of the maximum will depend on the nature of the system being investigated. The only prediction that can be made is that first-row heteroatoms will stabilize *either* a positively or negatively charged substrate more than its second-row counterparts when the charge on the substrate is small.

The connection between the magnitude of β and the stabilization of charged substrates made here is not a new one. As β decreases, the R–X bond energy decreases causing R–X to be more polarizable. The stabilization of charged substrates by the mixing of ground and excited states has been suggested by others.[17b] A new insight gained here is that in some cases a charged substrate will prefer the less polarizable first-row substituent over the more polarizable second-row substituent.



(C) Experimental Evidence. Both the ab inito MO calculations and the qualitative analysis predict that charged substrates may prefer a first-row substituent over the corresponding second-row substituent only when the charge on the substrate is small in magnitude. This situation will occur when the charge on the substrate is highly delocalized or solvated. This prediction alone is not surprising as the inverse relationship between substituent polarizability and solvent stabilization of a charged species has been noted.[18] However, examination of Figue 1 reveals that if a positively charged substrate prefers a first-row substituent, its negatively charged counterpart will not and vice versa.

It is known that gas-phase carbonium ions prefer second-row substituents and that this trend reverses in solution. However, carbanions prefer second-row substituents in solution and in the gas phase. This situation resembles that depicted in Figure 1A.

A similar situation is found for substituted benzoic acids. Benzoate anions prefer Cl over F in both the gas phase (Table V) and in solution (Table VI). However, fluorobenzoic acid is a stronger base in solution than its chlorosubstituted counterpart (Table VI). In this case we see that fluorine is better able to stabilize protonated benzoic acid than chlorine, but the opposite is found for the negatively charged benzoate anion.

Other cases where solvated cations prefer first-row substituents are found in Table VII. The substituted anilines and pyridines are stronger bases when substituted with first-row substituents. The preference for first-row substituents disappears when the charge on the substrate is localized; e.g., NCl_3 is known to be a stronger base than NCl_2F.[19]

Acetate anions prefer Cl over F in the gas phase (Table VIII). The reverse is true in solution (Table IX). We predict that chloroacetic acid will be found to be a stronger base than fluoroacetic acid. This is the opposite trend from that found for the benzoic acid; i.e., this situation resembles that found in Figure 1B,C.

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(18) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, 94, 4724 (1972).

(19) A. D. Craig, *Inorg. Chem.*, 3, 1628 (1964).