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Requirements and Interpretation of Linear Free Energy Relations

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Abstract: Why are free energies, which are composites of two quantities, ΔH and ΔS, with independent molecular explanations, often correlated with one or two parameters? This question is answered by describing a new functional relationship between ΔG and ΔH that leads to successful correlations. The analysis indicates why the more complex quantity ΔG is better fit by $b\beta$ parameters than the simpler quantity ΔH. Limitations of the correlations of ΔG with ΔH and $\Delta\nu_{OH}$ with ΔH are defined. The parameters resulting from the *E* and *C* fit of free energies and entropies can be reasonably interpreted in terms of the molecular contributions to the entropy.

Recently we have reported[1] that the *E* and *C* equation[2]

$$-\Delta H + W = E_A E_B + C_A C_B \qquad (1)$$

can be extended to include the spectral shifts which originally formed the basis of the Kamlet–Taft $b\beta$ approach.[3] We showed that for a general set of donors (acceptors), in which the specific interaction or spectral shift with an acceptor (or donor) was described by a C/E ratio other than 0.03, the data cannot be fit by $b\beta$ but can by *E* and *C*. This result shows that the $b\beta$ equation is a subset of eq 1 that is limited for general correlations to acceptors with a C/E ratio of 0.03. However, we have shown[1] that apparent fits for $b\beta$ can result for a C/E value other than 0.03 when a limited data set is used. The resulting correlation is without meaning, and one can predict which donors will not fit. We further showed that the concept of "family-dependent behavior"[3,4] often results when correlations are attempted with β in which the C/E ratio is not 0.03.

This $b\beta$ equation is reported to correlate free energies of hydrogen-bonding systems successfully. This fact, coupled with reports of linear $-\Delta H$ vs. ΔS relations, led us to investigate the utility of the *E* and *C* equation in the correlation of free energies. New insights involving requirements for free energy correlations and the molecular changes contributing to ΔG result from this work.

Free energies have contributions from two effects, ΔH and ΔS, that have independent molecular explanations. The success of the Hammett equation in fitting free energies is attributed to either a constant contribution of ΔS to ΔG or to entropy contributions that vary linearly with the enthalpies.[5] For systems in which such relations exist a ready incorporation of ΔG into the *E* and *C* model would result. However, there are known examples in which the enthalpies and entropies of coordinate bond formation do not obey either of these simple relationships. An example is the ΔH, ΔS, and ΔG of 4-fluorophenol adduct formation.[3] Plots of ΔS vs. ΔH, ΔG vs. ΔH, and ΔG vs. ΔS show no general linear behavior for a wide range of donor types. However, the ΔH values fit *E* and *C*, and since the $\Delta G°$'s are linear with β they should fit *E* and *C*. The explanation of these relationships should provide new insights into the requirements for linear free energy correlations and a molecular interpretation of free energies.

One of the advantages of a two-term equation (such as *E* and *C*) over simple linear models is that the requirement of linearity of ΔH and ΔS to fit the ΔG is lifted. It is sufficient that the entropy is affected by the same type of effects contained in the E_B and C_B parameters for coordinate bond formation enthalpies. If this is the case, the entropies can be fit to eq 1 with a different set of $E_A{}^*$ and $C_A{}^*$ parameters than those for ΔH. (The starred values indicate an acid parameter to fit entropies or free energies.[6]) Linearity of ΔH and ΔS is actually a highly restricted case of this; it implies that the $C_A{}^*/E_A{}^*$ ratio of ΔS is identical with the C_A/E_A ratio of ΔH. An excellent illustration of this argument is the comparison of the shift of the OH stretching frequency of phenol ($\Delta\nu_{OH}$) upon adduct formation to the enthalpy of phenol–base adduct formation. The values of $\Delta\nu_{OH}$ plotted vs. the corresponding ΔH are not linear for all bases. Sulfur donors deviate from a line described by donors with lower C_B/E_B ratios.[7] However, both $\Delta\nu_{OH}$ and ΔH fit the *E* and *C* equation (1), but the $C_A{}^*/E_A{}^*$ ratio of $\Delta\nu_{OH}$ is 0.15, different than the C_A/E_A ratio of 0.10 for ΔH. This interpretation[1] of the ΔH and $\Delta\nu_{OH}$ relations has finally laid to rest the controversies[8] regarding ΔH vs. $\Delta\nu$ relations.

In this paper we offer a successful fit of free energies, entropies, and enthalpies of iodine and 4-fluorophenol adducts to eq 1 and indicate conditions that will cause the relations to fail. We provide new insights for successful free energy correlations. Finally, the understanding of which spectral shifts and equilibrium constants fit the *E* and *C* model is an important result for it simplifies the extension of *E* and *C* to a wider number of donors because free energies and spectral shifts are much easier to measure than enthalpies. However, when enthalpy data and free energies or spectral shifts give conflicting parameters, the former are preferred because of their more direct relation to coordinate bond strengths.

Results and Discussion

The acceptors chosen for this study are iodine and 4-fluorophenol. The thermodynamics of adduct formation with both acceptors have been studied extensively, and a large amount of data are available. Both acceptors are part of the original *E* and *C* fit,[2,9] and the reported E_A and C_A parameters are well-defined because the acids have been studied with a wide range of donor types (varying C_B/E_B ratios).[10] Furthermore, these two acids represent extremes in the nature of the donor–acceptor interaction: the iodine interaction is dominated by covalency ($C_A/E_A = 1$) while 4-fluorophenol is dominated by electrostatic bonding ($C_A/E_A = 0.11$).[2]

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Table I. Fits of Free Energies and Entropies for I_2 and 4-Fluorophenol Adducts of Various Bases to the *E* and *C* Equation

I_2					4-fluorophenol				
donor	$-\Delta G_{\text{exptl}}{}^{298}$	$-\Delta G_{\text{calcd}}{}^{298\,a}$	$-\Delta S_{\text{exptl}}$	$-\Delta S_{\text{calcd}}{}^{b}$	donor	$-\Delta G_{\text{exptl}}{}^{298}$	$-\Delta G_{\text{calcd}}{}^{298\,c}$	$-\Delta S_{\text{exptl}}$	$-\Delta S_{\text{calcd}}{}^{d}$
pyridine	3.18[f]	3.42	15.5	14.0	DMF	2,81	2.95	11.5	11.0
methylamine	3.43[f]	3.30	12.3	13.1	DMA[h]	3.29	3.48	11.3	10.7
ethylamine	3.75	3.48	12.3	13.2	ethyl acetate	1.49	1.41	10.9	11.3
diethylamine	4.22[f]	4.38	18.4	18.0	acetone	1.60	1.53	11.9	12.0
diethyl ether	1.12[f]	1.35	10.3	9.5	diethyl ether	1.38	1.47	15.5[e]	14.5
p-dioxane	1.30[f]	1.03	7.3	8.1	THF	1.70	1.64	14.8	14.6
THF	1.70[f]	1.95	11.6	11.1	Me_2SO	3.65	3.62	10.9	10.9
THP	1.66[f]	1.70	10.7	10.5	pyridine *N*-oxide	3.75	3.76	12.9	13.1
diethyl sulfide	3.08[f]	2.89	15.9	16.5	HMPA	4.85	4.73	10.6	11.0
THTP	3.19[f]	3.14	17.1	17.3	triethylphosphate	3.73	3.65	9.4	9.5
triethylamine[e]	5.01[f]	5.83	23.5	21.3					

[a] Calculated from $-\Delta G^\circ = 1.31E_B + 0.567C_B - 1.81$, $r = 0.980$.[g] [b] Calculated from $-\Delta S = -1.16E_B + 1.50C_B + 5.77$, $r = 0.973$.[g] [c] Calculated from $-\Delta G^\circ = 5.81E_B + 0.855C_B - 4.40$, $r = 0.996$,[g] $s = 0.11$ kcal mol^{-1}. [d] Calculated from $-\Delta S = 4.99E_B + 1.29C_B + 13.94$. $r = 0.973$,[g] $s = 0.34$ eu. [e] Point left out of fit; steric contribution may enhance entropy. [f] ΔG_{298} calculated from the reported ΔG and ΔS. [g] These empirical equations constitute the best fit of the data. [h] DMA = dimethylacetamide.

Since solvent reorganization accompanying adduct formation is a potential contributor to ΔS, the selection of data to be fit is very important for ΔG correlations. Contributions of donor nonideality to ΔG have been described.[9] For 4-fluorophenol, the $-\Delta G$'s are determined[11] by ^{19}F NMR in CCl_4, and the $-\Delta H$'s are those determined by Arnett et al.[8] calorimetrically, also in CCl_4. Thus, ΔS is determined by the difference between independent measurements. This gives a good data set as all of the thermodynamic parameters are determined by using the same solvent. This choice of data limits the ΔG correlation to oxygen bases because *E* and *C* is set up to correlate enthalpies of pyridines and amines in hexane, not CCl_4.[12,13] The data base selection is not as clear for the I_2 acceptor. Almost all the thermodynamic data come from the use of van't Hoff plots of spectrophotometric data and therefore relate errors in ΔH to ΔS. Most of the reliable data for polar oxygen donors use CCl_4 as the solvent[9] while data for other donors were determined in hexane. Only free energies obtained for slightly polar donor molecules in the solvent hexane are used.[14-18] The free energies and entropies for these are to be fit to eq 1 using the reported E_B and C_B values in order to determine if these quantities can be related to parameters that predict the enthalpies.

The results of the two fits of $-\Delta G^\circ$ for adduct formation are given in Table I. Both the iodine and 4-fluorophenol free energies fit the *E*, *C*, and *W* equation (*W* for a donor independent contribution) well, though not quite as well as the enthalpies. When the $E_A{}^*$ and $C_A{}^*$ parameters of the free energy fits are compared to the published E_A and C_A parameters[2] for ΔH, it can be seen that the addition of the entropy term in $-\Delta G$ causes $C_A{}^* < C_A$ and $E_A{}^* > E_A$. In contrast to a C_A/E_A ratio of 0.11 for the enthalpy of 4-fluorophenol adduct formation, the $C_A{}^*/E_A{}^*$ ratio of the free energy is 0.015. We have shown[1] that only when the $C_A{}^*/E_A{}^*$ ratio of the system is ~0.03 will one obtain linear plots with β for a wide range of donor types. This accounts for the report that better correlations of ΔG than ΔH are obtained in plots vs. β when a wide range of donors is employed. The *E* and *C* fit of the entropies is also shown in Table I. Since the *C*/*E* ratio for the enthalpies differs from that of $C_A{}^*/E_A{}^*$ for the entropies, we also understand the reason plots of ΔS vs. ΔH are not linear for a wide range of donors. At room temperature, the $T\Delta S$ term is smaller than $-\Delta H$, and as a result a poorer fit of the entropy data than that of the enthalpy data still provides a reasonable fit of ΔG.

Because of the fact that the ΔH's of these systems are part of the original data set of *E* and *C*, the correlations are biased toward the ΔH part of ΔG. This, unfortunately, tends to lump the errors of a ΔG fit into the $T\Delta S$ term, leading to a much poorer fit then might be reasonably expected. A simple 0.1 kcal/mol error in ΔH can lead to a 0.3 eu miss of the corresponding ΔS.

It is significant that $-\Delta G$ and ΔS can be fit to eq 1 by using the E_B and C_B parameters derived from the fit of the enthalpies. For such systems, this indicates that a functional relationship exists between entropies of adduct formation and enthalpies of adduct formation even when the quantities are not linear. We can understand the dependence of ΔS on ΔH and the results of our fit by employing arguments similar to those offered earlier by Person[19] to account for the linear relation between ΔH and ΔS in some systems. The ΔS fits for I_2 and 4-fluorophenol show that a large part of the entropy is independent of the donor, the constant *W* term. This negative contribution to ΔS is mainly a donor-independent loss of rotational and translational freedom accompanying the combination of the donor and acceptor into one molecule, the adduct. A smaller, positive contribution to ΔS results from the gain of six vibrational degrees of freedom accompanying the simple coupling of the two molecules together (3N − 6 rule).

Our next concern is the donor dependent (E_B/C_B) contributions to ΔS which arise primarily from the vibrational term.[19] For very weak complexes the new vibrational degrees of freedom will be similar to the translational and rotational degrees of freedom from which they came, $\Delta S(\text{vib}) \approx +40$ eu.[19] For strong complexes, $\Delta S(\text{vib}) \approx 0$ eu. The entropy contribution from the *E* and *C* fit is positive (a decrease in $-\Delta S$) in the E_A parameter while it is negative in the C_A parameter (an increase in $-\Delta S$). An electrostatic interaction (E_AE_B) can be viewed as inducing small changes in the force constants of the donor and acceptor vibrations. Covalency in the interaction (C_AC_B) tends to change the electron distribution within the molecule so that the strength of the new bond often occurs at the expense of the bonds within the donor and acceptor molecules. For example, the O–H bond of phenol and I–I bond of iodine lengthen and weaken when adducts are formed. This causes a negative change in ΔS which counteracts the change in the *E* term.

There are noticeable deviations in the *E* and *C* fit of the entropies of adduct formation. Most of these may be attributed to simple effects such as the steric restriction of internal rotational modes of the donor (such as triethylamine) or acceptor upon complexation. However, acetonitrile and its derivative, chloroacetonitrile, miss badly in the I_2 data, and acetonitrile also misses for the 4-fluorophenol prediction. These deviations all produce a more negative calculated ΔS than experimental. This is similar to the $\Delta\nu_{OH}$ fits, in which donors such as benzene have a much

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smaller effect than *E* and *C* predicts. There very likely is a "window" of bond strengths in which the log of the stretching force constant changes in the adduct can be fit to *E* and *C*. For very weak adducts, *E* and *C* probably overestimates the covalent perturbation to the existing bonds, causing these systems to miss the predictions of the correlations. The calculated and experimental results in CCl_4 for the Et_2S adduct of 4-fluorophenol are also in conflict as the calculated entropy is ~10 eu too large. This may be due to complexation of the solvent with this donor[8] as well as the effect described above.

The changes we have observed in the *E* and *C* fits of entropies and free energies are seen to be reasonable when compared to physical models for these effects. Furthermore, we have demonstrated that in order to obtain a free energy correlation with an *E* and *C* type of model the condition is that both the enthalpy and entropy fit an equation of the *E* and *C* form. It is not necessary that ΔS be a linear function of ΔH, for linearity would be require that ΔH and ΔS have the same C_A/E_A ratio. We emphasize that ΔG correlations should only be carried out with data from a given solvent that does not interact with the reagent being varied (donors in the above case). Even under these conditions the discussion given indicates why exceptions may still occur in ΔG fits.

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Registry No. Iodine, 7553-56-2; 4-fluorophenol, 371-41-5.

Rearrangement and Fragmentation Processes in the Methanethiol and Dimethyl Sulfide Radical Cations

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Abstract: Ab initio molecular orbital calculations with large, polarization basis sets and incorporating electron correlation have been used to examine aspects of the CH_3S^+, $CH_4S^{+\cdot}$, and $C_2H_6S^{+\cdot}$ potential-energy surfaces. Detailed comparisons are drawn with corresponding CH_3O^+, $CH_4O^{+\cdot}$, and $C_2H_6O^{+\cdot}$ systems. The most stable CH_3S^+ ion is clearly the mercaptomethyl cation, CH_2SH^+ (**1**). Triplet thiomethoxy cation, CH_3S^+ (**2**), lies significantly higher in energy, while singlet thiomethoxy cation (**3**) is found to rearrange without activation energy to CH_2SH^+. For the $CH_4S^{+\cdot}$ system, the calculations reveal two stable isomeric ions, namely, the well-known methanethiol radical cation, $CH_3SH^{+\cdot}$ (**5**), and the recently discovered methylenesulfonium radical cation, $CH_2SH_2^{+\cdot}$ (**6**). The latter is calculated to lie 76 kJ mol^{-1} higher in energy than **5**, with a barrier to rearrangement to **5** of 114 kJ mol^{-1}. Both **5** and **6** will form CH_2SH^+ upon loss of H·. Examination of the relevant part of the $C_2H_6S^{+\cdot}$ potential-energy surface establishes a rearrangement–dissociation mechanism for the production of CH_3S^+ ions of structure CH_2SH^+ from ionized dimethyl sulfide, $CH_3SCH_3^{+\cdot}$ (**10**). This involves initial formation of a sulfonium ion intermediate, $CH_2SHCH_3^{+\cdot}$ (**11**), which subsequently undergoes simple bond cleavage. The CH_2SH^+ ion produced via this process has little excess energy. The intermediate sulfonium ion (**11**) lies 82 kJ mol^{-1} above $CH_3SCH_3^{+\cdot}$ (**10**), with a barrier to rearrangement to **10** of 120 kJ mol^{-1}, and represents a new, stable $C_2H_6S^{+\cdot}$ isomer.

Introduction

For many years, there has been considerable interest in the ionization and subsequent fragmentation of organosulfur compounds. The ion which has probably attracted most attention is CH_3S^+.[2-15] Earlier studies considered two structural isomers: CH_3S^+, thought to be generated[2-4,6-8] by ionization and fragmentation of alkyl methyl sulfides (CH_3S–R), and CH_2SH^+, thought to be generated[5-9] by ionization and fragmentation of alkane thiols (R–CH_2SH). In this way, CD_3SH was considered[6,7] to produce both ions, viz., CD_3S^+ and CD_2SH^+, by H· and D· loss, respectively. The heats of formation ($\Delta H_f{}^{\circ}{}_{298}$) of CH_3S^+ and CH_2SH^+ were reported[6] to be 895 and 920 kJ mol^{-1}, respectively.

However, recent studies[10-15] have cast doubt on the existence of an ion with the CH_3S^+ structure of energy similar to that of CH_2SH^+. The key observation was made by McLafferty and co-workers,[10,16] who combined the techniques of collisional-activation mass spectrometry and ab initio molecular orbital theory to investigate the CH_3S^+ and CH_3O^+ systems. Contrary to expectations, they found that, on fragmentation at low ionizing-electron energies, the dimethyl sulfide and dimethyl ether radical cations ($CH_3XCH_3^{+\cdot}$, X = S, O) yield the mercaptomethyl and

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