JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 7, 403–411 (1994)

σ–π AND n–π STABILIZATION ENERGIES IN VINYL AND PHENYL COMPOUNDS

YU-RAN LUO AND JOHN L. HOLMES

Department of Chemistry, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada

A means for determining the stabilization energies, E_c(X), resulting from σ–π and n–π interactions in vinyl and phenyl compounds is described. It is based on extensions of the additivity principle for thermochemical data for organic compounds. The results also provide a method for predicting heats of formation of unsaturated compounds from those of (known) saturated analogues. It is shown that there is a linear relationship between the stabilization energies E_c(X) and the Hammett substituent constants σ_p^+(X). The new results have been used to predict the heats of formation of a number of saturated and unsaturated Si-, Ge-, Sn-, P-, As-, Se-, Zn-, Cd- and Hg-containing species.

INTRODUCTION

The interactions between the substituent X in vinyl-X and phenyl-X compounds and the double bond and the benzene ring, respectively,[1] are identified as 'stabilizing' when the enthalpy change for the isodesmic reaction

$$C_2H_4 \text{ (or } C_6H_6) + \text{Alkyl-X} \rightarrow C_2H_3X \text{ (or } C_6H_5X) + \text{Alkyl-H} \quad (1)$$

is negative. The double-bond stabilization energy of the hydroxyl group has recently been estimated[1a] to be $-8\cdot1 \pm 0\cdot6$ kcal mol^{-1} (1 kcal = 4·184 kJ) by considering data from seven gas-phase experiments.

There are few experimental values for the heats of formation of vinyl compounds[2] and so any method for predicting their heats of formation is a useful addition to organic thermochemistry. Recently, a simple relationship between the heats of formation for 37 pairs of vinyl and phenyl derivatives has been described:[3]

$$\Delta_f H^\circ(C_2H_3X) = \Delta_f H^\circ(C_6H_5X) - 7\cdot1(\pm 1\cdot5) \text{ kcal mol}^{-1} \quad (2)$$

In the present work, this result will be used to estimate the stabilization energies arising from σ–π and n–π interactions in vinyl-X and phenyl-X compounds. The ensuing relationship can be used to predict the heats of formation of many unsaturated organic and organometallic compounds The term 'σ–π conjugative interaction' is preferred over 'hyperconjugation,' an old term in the chemistry literature.[1b] Other π–π and d–π conjugative interactions in unsaturated species, containing groups such as C=C—C=C, Ph—C=C and C=C—CH$_2$—CO, will be not discussed in this paper.

RESULTS AND DISCUSSION

In a series of papers, a new scale of electronegativity[4] or the covalent potential, V_x, has been used to correlate, analyze and predict the homolytic and heterolytic bond dissociation energies (BDEs) of X—C bonds in saturated and unsaturated organic compounds, the heats of formation of organic neutral and ionized species and molecular energetics.[4–11] A good linear relationship between the differences of $\Delta_f H^\circ(CH_3X)$ and $\Delta_f H^\circ(C_2H_5X)$ and v_x was found.[5a] However, there is not a similar linear correlation[3] between the differences of $\Delta_f H^\circ(CH_3X)$ and $\Delta_f H^\circ(C_2H_3X)$ versus V_x. There are two major anomalies, for CH$_3$ and OH groups, as shown in Figure 1 in Ref. 3. Conventionally, the two anomalies may be explained as resulting from a strong, characteristic interaction between the π systems and the adjacent substituent X.[1,12] This interaction for the CH$_3$ group arises from σ–π conjugative interaction,[1d] that is, the overlap between the σ orbital of the C—H bonds in the CH$_3$ group and the π orbital of the adjacent C=C double bond, while that of the OH group is due to n–π conjugative interaction, i.e. the overlap between the n orbital of the lone-pair electrons in the OH group and the π orbital of the adjacent C=C double bond. The same explanation applies to the phenyl group.

CCC 0894–3230/94/080403–09

Received 26 August 1993
Revised 25 March 1994

Stabilization energies in substituted vinyl and phenyl compounds

For saturated compounds, such as C_2H_5X, the above-mentioned conjugative interaction does not exist. The heats of formation of many ethyl derivatives, $\Delta_f H^\circ(C_2H_5X)$, are particularly reliably known.[2,13] It is proposed that the enthalpy change of the following isodesmic reactions (3) and (4), which produce vinyl-X and phenyl-X, may be used to determine the stabilization energies, arising from $\sigma-\pi$ and $n-\pi$ conjugative interactions, E_c, in vinyl and phenyl compounds:

$$\text{Ethyl-X} + \text{Vinyl-H} \rightarrow \text{Ethyl-H} + \text{Vinyl-X} \qquad (3)$$

$$\text{Ethyl-X} + \text{Phenyl-H} \rightarrow \text{Ethyl-H} + \text{Phenyl-X} \qquad (4)$$

$$\begin{aligned} E_c(\text{vinyl-X}) \equiv \Delta H(\text{vinyl-X}) &= \Delta\Delta_f H^\circ(C_2H_3X/C_2H_5X) \\ &\quad + \{\Delta_f H^\circ(C_2H_6) - \Delta_f H^\circ(C_2H_4)\} \\ &= \Delta\Delta_f H^\circ(C_2H_3X/C_2H_5X) \\ &\quad - 32\cdot5 \pm 0\cdot3\ \text{kcal mol}^{-1} \qquad (5) \end{aligned}$$

$$\begin{aligned} E_c(\text{phenyl-X}) \equiv \Delta H(\text{phenyl-X}) \\ &= \Delta\Delta_f H^\circ(C_6H_5X/C_2H_5X) \\ &\quad + \{\Delta_f H^\circ(C_2H_6(- \Delta_f H^\circ(C_6H_6)\} \\ &= \Delta\Delta_f H^\circ(C_6H_5X/C_2H_5X) \\ &\quad - 39\cdot7 \pm 0\cdot3\ \text{kcal mol}^{-1} \qquad (6) \end{aligned}$$

where

$$\Delta\Delta_f H^\circ(C_2H_3X/C_2H_5X) = \Delta_f H^\circ(C_2H_3X) - \Delta_f H^\circ(C_2H_5X) \qquad (7)$$

$$\Delta\Delta_f H^\circ(C_6H_5X/C_2H_5X) = \Delta_f H^\circ(C_6H_5X) - \Delta_f H^\circ(C_2H_5X) \qquad (8)$$

Using equation (2), we can write

$$E_c(\text{vinyl-X}) = E_c(\text{phenyl-X}) \equiv E_c(X) \qquad (9)$$

Equation (9) states that the stabilization energies in vinyl and phenyl compounds are transferable parameters which depend only on the nature of the substituent X. Hence the thermochemical data for phenyl compounds available in Refs 2 and 13 can be used to estimate the stabilization energies E_c(vinyl-X), and vice versa.

It should be emphasized that the stabilization energy, $E_c(X)$, is a relative energy, as described in Ref. 1a. $E_c(X)$ consists of two parts, one arising from the enthalpy change accompanying replacement of H by X in the standard or reference species (here, ethyl derivatives). This general approach involving isodemic substitutions has been discussed previously for saturated compounds.[4] The second are the corresponding enthalpy changes in the vinyl and phenyl derivatives. The $E_c(X)$ values derived from equations (5) and (6) are ascribed to the $\sigma-\pi$ and $n-\pi$ interactions in the unsaturated compounds.

Using equations (5) and (6) and the experimental data

Table 1. Values for $\Delta\Delta_f H^\circ(C_2H_3X/C_2H_5X)$ and E_c(vinyl-X) (kcal mol^{-1})

X	$\Delta_f H^\circ(C_2H_3X)$[a]	$\Delta_f H^\circ(C_2H_5X)$[b]	$\Delta\Delta_f H^\circ(C_2H_3X/C_2H_5X)$	E_c(vinyl-X)
(1) Alkyl with $\sigma-\pi$ interaction				
CH_3	4·8 ± 0·2	−25·0 ± 0·1	29·8 ± 0·3	−2·7 ± 0·5
C_2H_5	0 ± 0·3	−30·0 ± 0·2	30·0 ± 0·4	−2·5 ± 0·6
n-Pr	−5·1 ± 0·3	−35·1 ± 0·3	30·0 ± 0·4	−2·5 ± 0·6
i-Pr	−6·6 ± 0·2	−36·7 ± 0·3	30·1 ± 0·4	−2·4 ± 0·6
n-Bu	−10·4 ± 0·4	−39·9 ± 0·2	29·5 ± 0·5	−3·0 ± 0·7
s-Bu	−11·8 ± 0·4	−41·1 ± 0·3	29·3 ± 0·5	−3·2 ± 0·7
i-Bu	−12·3 ± 0·5	−41·8 ± 0·3	29·5 ± 0·6	−3·0 ± 0·8
t-Bu	−14·5 ± 0·4	−44·5 ± 0·3	30·0 ± 0·5	−2·5 ± 0·7
(2) C-centered groups with $\sigma-\pi$ interaction				
CH_2OH	−29·7 ± 0·5	−60·9 ± 0·2	31·2 ± 0·6	−1·3 ± 0·8
CH_2Cl	−1·3 ± 0·6	−31·6 ± 0·1	30·3 ± 0·7	−2·2 ± 0·8
CH_2Br	10·8 ± 1·1	−20·2 ± 0·1	31·0 ± 1·2	−1·5 ± 1·3
(3) O-centered groups with $n-\pi$ interaction				
OH	−30	56·3 ± 0·1	26·3 ± 1·2	−6·2 ± 1·3
OMe	−25·5	−51·7	26·2	−6·4 ± 2
OEt	−33·7 ± 0·3	−60·1 ± 0·1	26·4 ± 0·4	−6·1 ± 0·6
O-*s*-Pr	−42 ± 1	−69·2	27·2	−5·3 ± 2
OC_6H_5	5·4 ± 0·5	−24·3 ± 0·1	29·7 ± 0·6	−2·8 ± 0·8[c]
$CH_3C(O)O$	−75·3 ± 0·2	−106·1 ± 0·1	30·8 ± 0·3	−1·7 ± 0·5[c]

[a] Experimental values from Refs 2 and 13, or see Ref. 3, unless indicated.
[b] Experimental values from Refs 2 and 13.
[c] See discussion in text.

for $\Delta_fH^\circ(C_2H_3X)$, $\Delta_fH^\circ(C_6H_5X)$ and $\Delta_fH^\circ(C_2H_5X)$ from Refs 2 and 13, the values of E_c(vinyl-X) and E_c(phenyl-X) have been estimated and are listed in Tables 1 and 2, respectively. In this work, an error of ± 1 kcal mol^{-1} is used for heats of formation for which no error limits have been reported. In Table 2, the values of E_c(vinyl-X) and E_c(phenyl-X) are compared. The following results should be emphasized.

(1) The values of E_c(vinyl-X) and E_c(phenyl) are either negative or near zero, i.e. reactions (3) and (4) are exo- or neutrothermic, showing that σ–π and n–π effects in vinyl-X and phenyl-X compounds may thermodynamically stabilize these polyatomic systems.

(2) The values of E_c(vinyl-X) and E_c(phenyl) in Tables 1 and 2 are almost equal, within the experimental uncertainty, showing the reliability of equation (9).

(3) For X = alkyl, the σ–π stabilization energies, E_c(vinyl-X) and E_c(phenyl), are a constant, $-2{\cdot}7 \pm 0{\cdot}5$ kcal mol^{-1}, within the experimental uncer-

Table 2. Values for $\Delta\Delta_fH^\circ(C_6H_5X/C_2H_5X)$, E_c(phenyl-X) and E_c(X) (kcal mol^{-1})

				E_c(X)	
X	$\Delta_fH^\circ(C_6H_5X)$[a]	$\Delta_fH^\circ(C_2H_5X)$[b]	$\Delta\Delta_fH^\circ(C_6H_5X/C_2H_5X)$	Phenyl-X	Vinyl-X[d]
(1) Alkyl with σ–π interaction					
CH_3	12·0 ± 0·2	−25·0 ± 0·1	37·0 ± 0·3	−2·7 ± 0·5	−2·7 ± 0·5
C_2H_5	7·1 ± 0·3	−30·0 ± 0·2	37·1 ± 0·4	−2·6 ± 0·6	−2·5 ± 0·6
n-Pr	1·9 ± 0·2	−35·1 ± 0·3	37·0 ± 0·4	−2·7 ± 0·6	−2·5 ± 0·6
i-Pr	1·0 ± 0·3	−36·7 ± 0·3	37·7 ± 0·5	−2·0 ± 0·7	−2·4 ± 0·6
n-Bu	−3·1 ± 0·3	−39·9 ± 0·2	36·8 ± 0·4	−2·9 ± 0·6	−3·0 ± 0·7
s-Bu	−4·2 ± 0·4	−41·1 ± 0·3	36·9 ± 0·5	−2·8 ± 0·7	−3·2 ± 0·7
i-Bu	−5·1 ± 0·4	−41·8 ± 0·3	36·7 ± 0·5	−3·0 ± 0·7	−3·0 ± 0·8
t-Bu	−5·4 ± 0·4	−44·5 ± 0·3	39·1 ± 0·5	−0·6 ± 0·8[c]	−2·5 ± 0·7
c-C_3H_5	36·2 ± 0·2	−1	37 ± 1	−2·7 ± 1	
Bz	33 ± 0·7	1·9 ± 0·2	34·9 ± 0·8	−4·8 ± 1·0	
(2) C-centered groups with σ–π interaction					
CH_2OH	−24·0 ± 0·4	−60·9 ± 0·2	36·9 ± 0·5	−2·8 ± 0·7	−1·3 ± 0·8
CH_2Cl	4·5 ± 0·7	−31·6 ± 0·1	36·1 ± 0·8	−3·6 ± 1·0	−2·2 ± 0·8
CH_2Br	16 ± 0·5	−20·2 ± 0·1	36·2 ± 0·6	−3·5 ± 0·8	−1·5 ± 1·3
CH_2SH	22 ± 0·7	−16·2 ± 0·1	38·2 ± 0·8	−1·5 ± 0·9	
CH_2NH_2	20 ± 0·7	−16·8 ± 0·1	36·8 ± 0·8	−2·9 ± 0·9	
CH_2SCH_3	19·0 ± 0·7	−19·6 ± 0·2	38·6 ± 0·8	−1·1 ± 1·1	
CH_2OCH_3	−23·6 ± 0·8	−61·9 ± 0·2	38·3 ± 0·4	−1·4 ± 0·4	
(3) O-centered groups with n–π interaction					
OH	−23·0 ± 0·3	−56·3 ± 0·1	33·3 ± 0·4	−6·4 ± 0·6	−6·2 ± 1·3
OMe	−16·2 ± 0·3	−51·7 ± 0·1	35·5 ± 0·4	−4·2 ± 0·6[c]	−6·4 ± 2
OEt	−24·3 ± 0·2	−60·1 ± 0·1	35·8 ± 0·3	−3·9 ± 0·5[c]	−6·1 ± 0·6
O-*s*-Pr		−69·2			−5·3
OC_6H_5	12·4 ± 0·4	−24·3 ± 0·1	36·7 ± 0·5	−3·0 ± 0·7[c]	−2·8 ± 0·8[c]
$CH_3C(O)O$	−66·8 ± 0·6	−106·1 ± 0·1	39·3 ± 0·5	−0·4 ± 0·8[c]	−1·7 ± 0·5[c]
(4) S-centered groups with n–π interaction					
SH	26·9 ± 0·3	−11·1 ± 0·2	38·0 ± 0·4	−1·7 ± 0·6	
SCH_3	23·4 ± 0·3	−14·2 ± 0·3	37·6 ± 0·7	−2·1 ± 0·9	
SC_2H_5	18·4 ± 0·6	−20·0 ± 0·2	38·4 ± 0·7	−1·3 ± 0·9	
SC_6H_5	55 ± 0·7	18·4 ± 0·6	36·6 ± 1·0	−3·1 ± 1·2	
(5) N-centered groups with n–π interaction					
NH_2	20·8 ± 0·3	−11·3 ± 0·2	32·1 ± 0·4	−7·6 ± 0·6	
$NHCH_3$	20		(31 ± 1·0)[e]	−8·7 ± 1·0	
NHC_2H_5	13 ± 1	−17·4 ± 0·5	30·4 ± 1·2	−9·3 ± 1·3	
$N(Et)_2$	9·5	−22·1 ± 0·1	31·6 ± 1·0	−8·1 ± 1·2	
NHC_6H_5	52 ± 0·7	13 ± 1	39 ± 1·3	−0·7 ± 1·4[c]	

[a] Experimental values from Refs 2 and 13, or see Ref. 3, unless indicated.

[b] Experimental values from Refs 2 and 13.

[c] see discussion in text.

[d] see Table 1.

[e] Calculated using $\Delta_fH^\circ(EtNHMe)_{est} = -11 \pm 0{\cdot}5$ kcal mol^{-1} in Ref. 13.

tainty, and largely independent of the number of C—H bonds at the β-position, relative to the double bond.

(4) When X is a carbon-centered group containing a heteroatom, the σ–π stabilization energies E_c(vinyl-X) and E_c(phenyl-X) are about −2 ± 1 kcal mol^{-1}, slightly less than that for (3) above.

(5) When X represents an oxygen-centered group, the n–π stabilization energies lie within the range −4·2 to −6·4 kcal mol^{-1} and the average value is −5·8 ± 1·5 kcal mol^{-1}.

(6) When X is a nitrogen-centered group, the n–π stabilization energies are significantly more negative and are about −8 ± 1 kcal mol^{-1}.

There are five exceptions. The first four (X = *t*-Bu, OC_2H_5, OC_6H_5 and NHC_6H_5) arise from the steric repulsion effect for branched species. The suggestion of steric repulsion in $C_6H_5OC_2H_5$ seems not to be in accord with conventional wisdom, but molecular mechanics calculations (see below) indicate that such a repulsion is realistic.

The fifth exception of $CH_3C(O)O$-vinyl and $CH_3C(O)O$-phenyl arises from the interaction between the lone-pair electrons of the oxygen atom and the neighboring vinyl (or phenyl) group being overridden by the stronger conjugative effect of the neighboring carbonyl-π bond, which leads to a greater stabilization.

Halides

It is known that the C—X bond lengths of vinyl and phenyl halides are about 0·04 Å shorter than those of alkyl-X bonds[16] and the corresponding dipole moments are also smaller than those of the saturated compounds.[12a] These have been explained as arising from the effect of n–π interactions.[1,12] How large is this energy?

The recommended heats of formation for ethyl, phenyl and vinyl halides generally have similar uncertainties,[2,13] but the reliability of some of the values for the unsaturated compounds is open to question. The equation (2) differences for the fluorides, −5·5 ± 0·6 kcal mol^{-1}, and bromides, −6·3 ± 1·2 kcal mol^{-1}, are in adequate agreement with the mean value (−7·1 ± 1·5 kcal mol^{-1}), but that for the chlorides is significantly different, −3·5 ± 0·5 kcal mol^{-1}.

The corresponding E_c values for vinyl chloride and bromide are 3·2 ± 0·5 and 1·2 ± 0·7 kcal mol^{-1}, whereas for the phenyl analogues the values are −0·5 ± 0·5 and 0·3 ± 1·3 kcal mol^{-1}, respectively. Positive E_c values are incompatible with stabilization and so further discussion of the available data is warranted.

For C_2H_3Cl, the $\Delta_f H^\circ$ proposed by Benson[14] is echoed in Ref. 13, namely 5 ± 1 kcal mol^{-1}. This is consistent with equation (2) (−7·4 ± 1 kcal mol^{-1}) and gives E_c = −0·7 ± 1 kcal mol^{-1}.

The heat of formation of vinyl iodide has only been measured indirectly,[15] but has been discussed in a few publications[3,14,15] and a selected value of 31·5 ± 1 kcal mol^{-1} is reasonable. The equation (2) result for the iodides is −7·9 ± 1·8 kcal mol^{-1} and the derived E_c values for C_2H_3I and C_6H_5I are 0·8 ± 1 and 1·5 ± 1·5 kcal mol^{-1}, respectively.

Finally, there is no experimental value for $\Delta_f H^\circ(C_2H_5F)$; this has been estimated[5a] to be −66·3 ± 0·5 kcal mol^{-1}; this leads to E_c values of 0·6 ± 1 and −1·1 ± 1 kcal mol^{-1} for vinyl and phenyl fluoride, respectively. As can be see in Table 3, the overall effect of halogen lies close to 0 kcal mol^{-1}.

Nitriles and nitro derivatives

CN and NO_2 are considered to be stronger electron-withdrawing groups than halogen, but the C—X bond

Table 3. Values for E_c(phenyl-X) and E_c(X) (kcal mol^{-1}) for X = halogen, NO_2 and CN

	$\Delta_f H^\circ$ [a]			E_c(X)	
X	C_2H_3X	C_6H_5X	C_2H_5X	Vinyl	Phenyl
(1) X = halogen					
F	−33·2 ± 0·4	−27·7 ± 0·4	(−66·3 ± 0·5)[b]	(0·6 ± 1)	(−1·1 ± 1)
Cl	8·9 ± 0·3 (5 ± 1)[c]	12·4 ± 0·3	−26·8 ± 0·3	3·2 ± 0·5 (−0·7 ± 1)[d]	−0·5 ± 0·5
Br	18·9 ± 0·5	25·2 ± 1·0	−14·8 ± 0·4	1·2 ± 0·7	0·3 ± 1·3
I	(31·5 ± 1)[d]	39·4 ± 1·4	− 1·8 ± 0·4	(0·8 ± 1)[d]	(1·5 ± 1·5)[d]
(2) X = CN and NO_2, electron-withdrawing groups					
CN	43·2 ± 0·5	51·6 ± 0·5	12·3 ± 0·1	−1·6 ± 1	−0·4 ± 0·5
NO_2	9 ± 2	16·1 ± 0·2	−24·5 ± 0·1	0·9 ± 2	0·9 ± 0·5

[a] From refs 2 and 13, unless indicated. The values in parentheses are all estimated, see text.
[b] Estimated, see Ref. 5a.
[c] Refs 13 and 14.
[d] See discussion in text.

lengths and the dipole moments of the vinyl and phenyl species, relative to the saturated compounds, are almost unchanged.[12a,16] Hence it has been assumed that there is almost no stabilization effect, as in the halides.[12a] For nitriles (see Table 3), $E_c(CN)$ is negative, supporting the presence of a stabilization effect. The effect of the nitrile function in ionic and radical species has been discussed elsewhere.[17] Table 3 gives small positive values for $E_c(NO_2)$ in keeping with virtually no stabilization within nitrobenzene. It is worth noting that for alkyl-substituted aromatic molecules the $E_c(NO_2)$ values remain close to zero, e.g. using data from Ref. 2, the E_c values for toluene and 2- and 4-ethylbenzene are $-0{\cdot}2 \pm 1{\cdot}3$, $0{\cdot}0 \pm 1{\cdot}6$ and $-1{\cdot}0 \pm 1{\cdot}6$ kcal mol^{-1}, respectively. Any effect for the nitro group must arise from π–π interactions, there being neither lone-pair electrons nor sigma electrons at the N atom. The same reasoning may explain the absence of a σ–π or n–π interaction in nitriles. The π–π conjugative interactions in nitrobenzene, nitriles, buta-1,3-diene and similar species are beyond the scope of this paper.

Sequence of the σ–π and n–π interaction energies

From the E_c values in Tables 1, 2 and 3, the trends of the σ–π and n–π stabilization in vinyl-X and phenyl-X species can readily be seen.

(1) For n–π stabilization across the Periodic Table, the sequence is N-centered > O-centered ≫ halogens, showing that the E_c values depend on the number of lone-pair electrons in X. The n–π stabilization is greatest, -7 to -9 kcal mol^{-1}, when X is an N-centered group. It is about zero for X = halogen and O-centered groups lie between them. Hence this stabilization follows the sequence one lone pair > two lone pairs ≫ three lone pairs.

(2) For n–π stabilization of O- and S-centered groups, we have O-centered > S-centered.

Note that the above trends are the same as those for the Hammett substituent constants. There is a linear relationship between the constants $\sigma_p^+(X)$ and the $E_c(X)$ values for 29 substituents X, for species which do not contain any steric effect, in Tables 1, 2 and 3, as

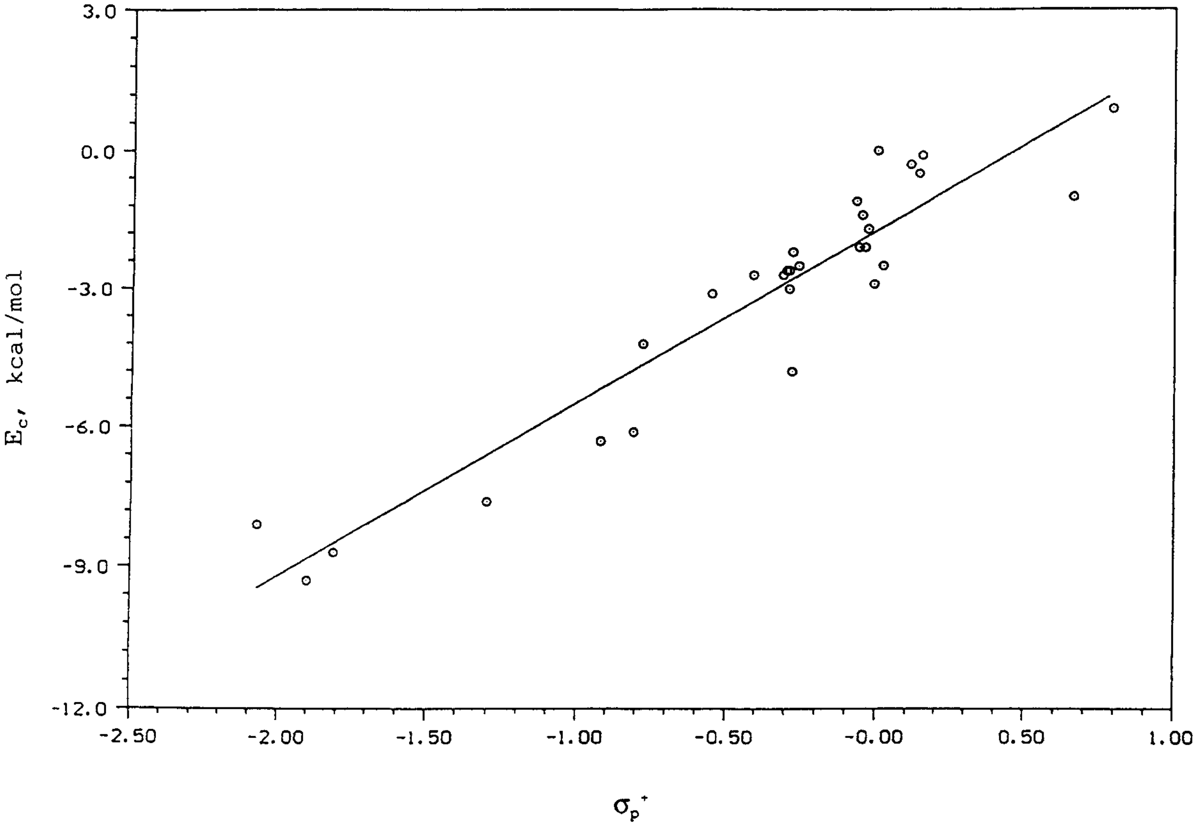

Figure 1. Relationship between the Hammett constant σ_p^+ and the stabilization energy E_c (kcal mol^{-1})

shown in Figure 1. This straight line can be expressed as

$$E_c(X) = 3{\cdot}84(\pm 0{\cdot}30)\sigma_p^+(X) - 1{\cdot}59(\pm 0{\cdot}23) \text{ kcal mol}^{-1} \quad (10)$$

Here the $\sigma_p^+(X)$ values are all from Ref. 18. The average and standard deviations of the fit are 0·8 and 1·0 kcal mol^{-1}, respectively, and the correlation coefficient is 0·924. Considering the uncertainties of the Hammett correlation and the thermochemical data, the relationship appears to be sound.

The $\sigma_p^+(X)$ values of more than 200 substituents X are available.[18] Equations (5), (6) and (10), therefore, provide an opportunity to estimate the heats of formation of a large number of vinyl, phenyl and other unsaturated compounds.

Relationships between heats of formation for important organic species

Although more than six million organic compounds have been characterized, heats of formation have been reliably experimentally measured for less than 4000.[2,13,19] *Ab initio* molecular orbital theory calculations, density function theory, a variety of semi-empirical methods and molecular mechanics all are available, but the empirical group additivity rule developed by Benson[14] and co-workers over the last 30 years provides the simplest and most useful method for obtaining heats of formation for a very wide range of organic and organometallic compounds.[20] Although many group additivity terms have been established, there is always room for more and the relationships described in Refs 3 and 5a and in this work provide useful supplements. Recent work is represented in Figure 2, which interrelates equations (2), (5) and (6) in this work and earlier equations (11,[5a] 12a[5d] and 12b[5d]) which respectively relate heats of formation for saturated compounds to the reliably known $\Delta_f H^\circ(CH_3\text{-}X)$ values[4] and relate heats of formation for saturated compounds to unsaturated compounds:

$$\Delta_f H^\circ[C(CH_3)_m H_{3-m}\text{-}X] = \Delta_f H^\circ(CH_3\text{-}X) + [0{\cdot}9 - 1{\cdot}5m(m-1)] - m\frac{V_x}{0{\cdot}67 + 0{\cdot}21m} \quad (11)$$

where m is the degree of methyl substitution and $m = 1$, 2 and 3 for primary, secondary and tertiary carbons atoms, respectively,

$$\Delta_f H^\circ(\text{allyl-X}) = \Delta_f H^\circ(\text{ethyl-X}) + 25{\cdot}2(\pm 0{\cdot}5) \text{ kcal mol}^{-1} \quad (12a)$$

and

$$\Delta_f H^\circ(\text{benzyl-X}) = \Delta_f H^\circ(\text{ethyl-X}) + 32{\cdot}0(\pm 1{\cdot}0) \text{ kcal mol}^{-1} \quad (12b)$$

Note that $\Delta_f H^\circ(CH_3\text{-}X)$ is the essential reference point and errors in this value will be carried forward into the scheme.

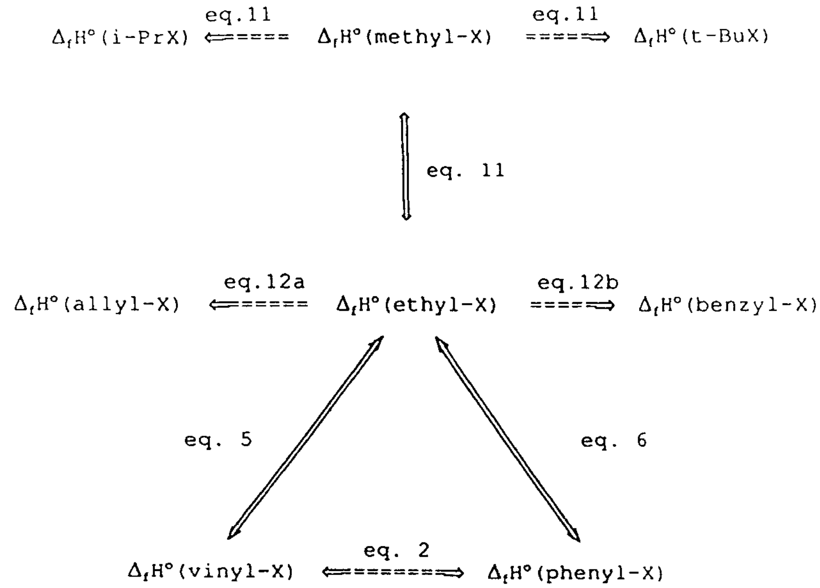

Figure 2. Relationship between equations involving heats of formation for important organic species

Prediction of heats of formation of organometallic compounds

By combining data from Figure 2 with Benson's group additivity data, heats of formation for a large number of organic and organometallic compounds can easily be predicted. Some examples are listed in Table 4. Their uncertainties are of the order of ±2–3 kcal mol^{-1}.

As an example, based on the observed heat of formation of CH_3SiH_3, $-7{\cdot}0 \pm 1{\cdot}0$ kcal mol^{-1},[21] and equation (11), we can predict

$$\Delta_f H^\circ(CH_3CH_2\text{-}SiH_3)_{est} = -10{\cdot}0 \pm 1{\cdot}5 \text{ kcal mol}^{-1}$$

Using equation (10, the E_c(Si-centered group) is about -1 kcal mol^{-1}, and from equation (6) we can further predict

$$\Delta_f H^\circ(C_6H_5\text{-}SiH_3)_{est} = 28{\cdot}7 \pm 2 \text{ kcal mol}^{-1}$$

This estimated value agrees with that predicted independently (27 kcal mol^{-1}) in Ref. 13.

Similarly, predicted heats of formation of many Si-, Ge-, Sn-, P-, As-, Se-, Zn-, Cd- and Hg-containing organometallic compounds are listed in Tables 4 and 5. Based on equation (10), the E_c values of SiH_3, SiF_3, $SiCl_3$ and $SiHCl_2$ are estimated to be about -1, 1, 0 and 0 ± 1 kcal mol^{-1}, respectively. The new $\Delta_f H^\circ$ estimates are compared with those reported in Refs 13 and 19. Note that most of the present estimated values in Table 4 agree with those in Refs 13 and 19, but two exceptions, ethyl-SiH_3 and vinyl-SiH_3, deserve mention. The two values recommended in Ref. 13 are incompatible, because in going from methyl-SiH_3 to ethyl-SiH_3 the heats of formation would be expected to decrease by a few kcal mol^{-1}, owing to the insertion of a CH_2 group. Using the group increment recommended by Walsh,[21] the value estimated for $\Delta_f H^\circ$(ethyl-SiH_3) becomes $-11{\cdot}0$ kcal mol^{-1}, consistent with that in this work (see Table 4). In addition, it is unreasonable that $\Delta_f H^\circ$(ethyl-SiH_3) 27 kcal mol^{-1} in Ref. 13, is more positive than $\Delta_f H^\circ$(vinyl-SiH_3), which in Ref. 13 is only 1 kcal mol^{-1}.

To examine further the predictive power of the

Table 4. Estimated $\Delta_f H^\circ$ of Si-, Ge-, Sn-, P-, As-, Se-, Zn-, Cd- and Hg-containing species (kcal mol^{-1})

	$\Delta_f H^\circ$					
X	CH_3-X[a]	Ethyl-X	Vinyl-X	Phenyl-X	Allyl-X	Benzyl-X
SiH_3	−7·0 ± 1[b]	−10·0 (27 ± 3)[e]	21·5 (1 ± 3)[e]	28·7 (27)[d]	15·2	22·0
SiF_3	−296[e]	−299	−268	−258 (−261)[d]	−274	−267
$SiCl_3$	−131[e]	−134 (−126 ± 6)[e]	−102 (−109)[d]	−94 (−95)[d]	−109	−102
$SiHCl_2$	−96 ± 2[e]	−99	−67	−59	−74	−67
GeH_3	4·6 ± 2·0	1·8	34·3	41·5	27·0	33·8
SnH_3	18·6 ± 2·0	16·3	48·8	56·0	41·5	48·3
PH_2[c]	−4·6 ± 1·5 (−4)[d]	−8·9	22	29 (31)[d]	16	23
AsH_2	8·1 ± 1·5 (11)[d]	4·2	36·7	43·9	29·4	36·2
SeH[f]	5·3 ± 1·0	0·4	33·9	41·1 (39)[d]	25·6	32·4
$ZnCH_3$[f]	13·1 ± 2[g]	12·2	45	52	37	44
$CdCH_3$[f]	25·8[g]	25·2	58	65	50	57
$HgCH_3$[f]	22·3 ± 1[g]	21·6	54	61	47	54
HgCl[f]	−12·3 ± 0·7[g]	−13·0 (−15·5 ± 1)[g]	20	27 (29·7)[e]	12	19
HgBr[f]	−4·4 ± 0·7[g]	−5·1 (−7·4 ± 1)[g]	27 (30)[d]	35 (38)[d]	20	27
HgI[f]	5·2 ± 0·4[g]	4·5 (3·3 ± 1)[g]	37	44	30	37

The values estimated in Ref. 6a, unless indicated.
[b] An experimental value from Ref. 21.
[c] Assuming the E_c value of PH_2 is about -2 kcal mol^{-1}, based on equation (10).
[d] The values estimated in Ref. 13.
[e] Observed in Ref. 13.
[f] Assuming that E_c(Zn-, Cd-, Hg- and Se-centered groups) is 0 kcal mol^{-1}.
[g] In Ref. 19.

Table 5. Estimated values of Δ_fH° of RMR, where M = Zn, Cd, Hg and Se (kcal mol^{-1})

	Metal atom[a]			
R	Zn	Cd	Hg	Se
Methyl				−4[b]
	(13·1 ± 2·0)[c]	(25·8 ± 0·3)[c]	(22·3 ± 1·0)[c]	
Ethyl	11·3	24·6	20·9	
	(13·6 ± 1·7)	(25·5 ± 0·7)	(17·8 ± 0·8)	(−14 ± 1)[c]
n-Propyl	1·3	14·6	10·9	−24
	(−2·9 ± 5·7)		(8·2 ± 1·4)	
Isopropyl	3·0	16·6	12·9	−27
			(9·7 ± 1·1)	
n-Butyl	−8·7	4·6	0·9	−34
	(−11·9 ± 5·8)		(−7·8 ± 1·8?)	
s-Butyl	−7·0	6·6	2·9	−37
Isobutyl	−12·7	0·6	−3·1	−38
			(−9·2 ± 1·8?)	
t-Butyl	−10·5	3·4	−0·3	−44
Vinyl	76	90	86	51
Phenyl	91	104	100	66
			(93·8 ± 1·5?)	(68·4 ± 1·2)
Allyl	62	75	71	36
Benzyl	75	89	85	50

[a] The values in parentheses are from Ref. 19.
[b] Estimated by the relationship in Figure 2.
[c] Reference points derived from Figure 2.

scheme described in Figure 2, some estimated heats of formation of organometallic compounds RMR, where M represents zinc, cadmium, mercury and selenium, are compared with experimental values from Ref. 19 (see Table 5). The few points with deviations >3 kcal mol^{-1} are those which are probably associated with incorrect thermochemical data; for example, it is not possible that the heat of formation of $(n\text{-Pr})_2\text{Hg}$, 8·2 kcal mol^{-1}, falls to −7·8 kcal mol^{-1} for $(n\text{-Bu})_2\text{Hg}$.

Steric effect

As has been emphasized many times,[4] Benson's group additivity rule fails for highly branched compounds owing to non-bonded steric repulsions. Equations (2), (5), (6), (11) and (12) will fail also when the non-bonded steric effect is significant. In Table 2, phenyl-*t*-Bu, phenyl-O-methyl, phenyl-O-ethyl, vinyl-O-phenyl, phenyl-O-phenyl and phenyl-NH-phenyl provide examples. Let us consider two examples. In the compounds $C_6H_5OCH_3$ and $C_6H_5OC_2H_5$, the closest distance between the *ortho-H* atom on the benzene ring and the H atom on the alkyd group is only 2·45 Å, according to calculations from the MM2 program. Hence the steric repulsion in $C_6H_5OCH_3$ and $C_6H_5OC_2H_5$ is not negligible and may be estimated to be about 2 kcal mol^{-1}. The steric repulsion energies could be 2–3 kcal mol^{-1} for the first five compounds, whereas for phenyl-NH-phenyl it could be as much as 8 kcal mol^{-1}.

We now return to the stabilization energy for vinyl-OH in the Introduction, −8·1 ± 0·6 kcal mol^{-1}.[1a] This stabilization energy was derived from the average for seven substituted vinyl-OH compounds, four of which were branched or highly branched. For these, a stabilization energy from −8·5 to −9·8 kcal mol^{-1} was reported. For the other three less substituted species, the range is from −5·3 to −7·0 kcal mol^{-1}, which is very close to those in Tables 1 and 2. The lengths of the C=C double bond and C—C single bond are about 1·4 and 1·54 Å in vinyl-X and ethyl-X, respectively. The smaller interatomic distance in vinyl compounds should result in larger non-bonded steric repulsions than in saturated compounds. According to the Scheme in Ref. 1a, the stabilization energy of highly branched vinyl compounds should be larger than that for unbranched analogues; hence the quoted E_c values must include the contribution from n–π interaction *and* from the steric effect (about 2–3 kcal mol^{-1}).

We suggest that a single E_c value for such stabilization should be used but in conjunction with appropriate corrections for steric effects. As can be seen in Tables 1 and 2, the average $E_c(\text{OH})$ value of −5·8 ± 1·5 kcal mol^{-1} agrees with those from Ref. 1a for all the least substituted vinyl alcohols.

CONCLUSION

A means to determine the stabilization energies, $E_C(X)$, arising from n–π and σ–π interactions can be established, based on extensions of the additivity principle for organic thermochemistry. There is a linear relationship between the stabilization energies and the Hammett substituent constants $\sigma_p^+(X)$. Equation (5) or (6) provides a bridge from the known heats of formation of saturated compounds to unknown heats of formation of unsaturated compounds, and can be used to predict the heats of formation of a number of saturated and unsaturated Si-, Ge-, Sn-, P-, As-, Se-, Zn-, Cd- and Hg-containing species.

ACKNOWLEDGMENTS

J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support. The authors are particularly grateful to Professor S. W. Benson for invaluable discussion.

REFERENCES

1. (a) J. R. Keeffe and A. J. Kresge, *J. Phys. Org. Chem.* **5**, 575 (1992); (b) J. B. Lambert and R. A. Singer, *J. Am. Chem. Soc.* **114**, 10246 (1992); (c) N. Muller and R. S. Mulliken, *J. Am. Chem. Soc.* **80**, 3489 (1958); (d) W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, p. 301. Wiley, New York, (1986).
2. J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd edn Chapman and Hall, London (1986).
3. Y. R. Luo and J. L. Holmes, *J. Phys. Chem.* **96**, 9568 (1992).
4. Y. R. Luo and S. W. Benson, *Acc. Chem. Res.* **25**, 375 (1992).
5. (a) Y. R. Luo and S. W. Benson, *J. Phys. Chem.* **92**, 5255 (1988); (b) **93**, 1674, 3304, 3306, 3791, 4643, 7333 (1989); **94**, 914 (1990); (c) Y. R. Luo and P. D. Pacey, *J. Phys. Chem.* **95**, 6745, 9470 (1991); (d) Y. R. Luo and J. L. Holmes, *J. Phys. Chem.* **98**, 303 (1994); (e) Y. R. Luo and J. L. Holmes, *J. Phys. Chem.* in press.
6. (a) Y. R. Luo and S. W. Benson, *J. Am. Chem. Soc.* **111**, 2486 (1989); (b) Y. R. Luo and P. D. Pacey, *J. Am. Chem. Soc.* **113**, 1465 (1991).
7. Y. R. Luo and S. W. Benson, *Inorg. Chem.* **30**, 1677 (1991).
8. Y. R. Luo and P. D. Pacey, *J. Phys. Org. Chem.* **4**, 562 (1991).
9. Y. R. Luo and P. D. Pacey, *Int. J. Mass. Spectrom. Ion Processes* **108**, 221 (1991); **112**, 63 (1992).
10. Y. R. Luo and P. D. Pacey, *Can. J. Chem.* **71**, 572 (1993).
11. Y. R. Luo and J. L. Holmes, *J. Mol. Struct. (Theochem.)* **281**, 123 (1993).
12. (a) G. W. Wheland, *Resonance in Organic Chemistry.* Wiley, New York (1955); (b) M. J. S. Dewar, *Hyperconjugation.* Ronald Press, New York (1962); (c) W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory.* Wiley, New York (1986); (d) T. H. Lowry, *Mechanism and Theory in Organic Chemistry*, 3rd edn. Harper and Row, New York (1987); (e) N. S. Isaacs, *Physical Organic Chemistry.* Wiley, New York (1987); (f) L. Klasinc and S. P. McGlynn in *The Chemistry of Double-Bonded Functional Groups, Part 1*, edited by S. Patai, p. 163. Wiley, Chichester (1989).
13. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
14. S. W. Benson, *Thermochemical Kinetics*, 2nd edn Wiley, New York (1976).
15. J. L. Holmes, *Int. J. Mass Spectrom. Ion Processes*, **118/119** 381 (1992).
16. H. J. M. Bowen *et al.* (Eds), *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publications No. 6 (1958) and No. 16 (1965). Chemical Society, London.
17. J. L. Holmes, F. P. Lossing and P. M. Mayer, *Chem. Phys. Lett.* **212**, 134 (1993).
18. C. Corwin, A. Leo and R. W. Taft, *Chem. Rev.* **91**, 165 (1991).
19. (a) J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds.* Academic Press, New York (1970); (b) J. B. Pedley and J. Rylance, *Sussex–N.P.L. Computer Analysed Thermochemical Organic and Organometallic Compounds.* University of Sussex, Brighton (1977).
20. (a) R. C. Reid, J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, 4th edn McGraw-Hill, New York (1987); (b) W. H. Seaton, E. Freedman and D. N. Treweek, *ASTM Data Series Publication, DS 51.* American Society for Testing and Materials, Philadelphia (1974); (c) E. S. Domalski and E. D. Hearing, *J. Phys. Chem. Ref. Data* **17**, 1637 (1989); (d) **22**, 805 (1993); (e) *NIST Estimation of the Thermodynamic Properties for Organic Compounds at 298.15 K.* NIST Thermodynamic Databases, Gaithersburg, MD (1990).
21. R. Walsh, in *The Chemistry of Organosilicon Compounds*, edited by S. Patai and Z. Rappoport, Chapt. 5. Wiley, Chichester (1989).