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“Thermochemical mimicry” of phenyl and vinyl groups: can it be extended to charged species?

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Abstract

By examination of a set of recently evaluated proton affinities, the thermochemical mimicry of phenyl and vinyl derivatives is shown not to apply to charged species. (Int J Mass Spectrom 179/180 (1998) 261–266) © 1998 Elsevier Science B.V.

Keywords: Enthalpy of formation; Ionization energies; Proton affinities; Substituent effects

1. Introduction

Some years ago it was asserted that there is a nearly constant enthalpy of formation difference for corresponding phenyl and vinyl derivatives [1]. That is, the quantity $[\Delta f H^0_m(g,\ C_6H_5X)\ - \Delta f H^0_m(g,\ C_2H_3X)]$ is numerically quite independent of the affixed X. Equivalently, the groups C_6H_5 and C_2H_3 may be said to be “homothermal pairs” [2] or “thermochemical mimics” [3]. This X-independent difference quantity (or, more precisely, the indifference to phenyl versus vinyl) was found [1] to equal ~30 kJ mol^{-1}. We denote this difference herein as $\delta H(X)$. The current article addresses some aspects of this thermochemical “rule of thumb” as applied to cationic affixed groups.

2. Effect of charged substituents

The current article addresses the effects of the substituent being charged. More precisely, let us examine whether the previously observed phenyl/vinyl regularity is also valid for protonated molecules. After all, were $[\Delta_f H^0_m(g,\ C_6H_5X)\ -\ \Delta_f H^0_m(g,\ C_2H_3X)] \equiv \delta H(X)$ essentially constant for all X and by inference for any affixed group, then $\delta H(X)$ should approximately equal $\delta H(XH^+)$ for all X/XH^+ pairs. Equivalently, we may assert the near equality

$$\Delta_f H^0_m(g,\ C_6H_5X) - \Delta_f H^0_m(g,\ C_6H_5XH^+) \approx \Delta_f H^0_m(g,\ C_2H_3X) - \Delta_f H^0_m(g,\ C_2H_3XH^+) \qquad (1)$$

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Dedicated to Professor Fulvio Cacace on the occasion of his 40th anniversary in ion science.

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Table 1
Proton affinities of C_6H_5X and C_2H_3X (protonation on X) in order of increasing values of the latter, and the derived difference quantity [a] $\delta PA(X)$ (in kJ mol^{-1})

X	$PA(C_6H_5X)$ [b]	$PA(C_2H_3X)$ [b]	$\delta PA(X)$
$CH_2^{\cdot}$	831.4	736.0	95.4
$O^{\cdot}$	857.7	774.0	83.7
$CHCH_2$	839.5	783.4	56.1
CN	811.5	784.7	26.8
CHO	834.0	797.0	37.0
$COOCH_3$	850.0	825.8	24.2
$C(CH_3)CH_2$	864.2	826.4	37.8
$COCH_3$	861.1	834.7	26.4
$CONH_2$	892.1	870.7	21.4
CH_2NH_2	913.3	909.5	3.8
CHNH	911.9	912.1	−0.2
4-C_5H_4N	939.7	944.1	−4.4
$CH_2N(CH_3)_2$	968.4	957.8	10.6

[a] It is implicitly assumed that the protonation site is the same for both phenyl and vinyl for a given X, namely on the X itself.

[b] All data are taken from [4].

By the addition of $\Delta_f H_m^0(g, H^+)$ to both sides of Eq. 1, we would thus deduce that

$$PA(C_6H_5X) \approx PA(C_2H_3X) \tag{2}$$

How valid is this relation? Despite the numerous species for which proton affinity values have been determined [4], there are surprisingly few cases for which Eq. 2 can be tested. Most often, protonation of the ring in the phenyl compound and/or protonation of the double bond in the vinyl compound is preferred over protonation on the group X and so the desired comparison is thwarted. Said differently, for those relevant X-protonated cases, the difference quantity $[PA(C_6H_5X) - PA(C_2H_3X)] \equiv \delta PA(X)$, is expected to be nearly constant with the numerical value of zero. Table 1 (in kJ mol^{-1}) gives the collection of so-defined group X's and the associated proton affinities for which meaningful comparison can be made.

It is immediately seen that the difference quantity is highly variable and generally very different from zero: it ranges from −4.4 to 95.4 kJ mol^{-1}. A posteriori, a significantly nonzero value is not particularly surprising. An ionic substituent may be expected to interact differently with phenyl and vinyl groups because a benzene ring and an olefinic double bond have different polarizabilities. Because each XH^+ group has its own geometry and "local" charge distribution, the resulting ion-induced dipole and ion-dipole stabilization will differ. The degree of conjugative delocalization varies for the various cations: $XH^+ = CH{=}NH_2^+$ is presumably strongly conjugating while $XH^+ = CH_2NH_3^+$ is reasonably expected to lack any π involvement with either phenyl or vinyl. Yet, for $CH{=}NH$ and CH_2NH_2—these polar, strongly basic X groups—protonation evidences a comparative indifference to what these groups are attached. We see that $\delta PA(X)$ varies over nearly 100 kJ mol^{-1}. $\delta H(XH^+)$ is thus not a constant or even roughly so.

Nonetheless, there is a rough pattern: those vinyl neutrals with the highest proton affinities of our collection [with X equal to the rather strongly basic nitrogenous groups CHNH, 4-C_5H_4N, CH_2NH_2, and $CH_2N(CH_3)_2$] have values of $\delta PA(X)$ that are within 10 kJ mol^{-1} of zero. On the other hand, those vinyl neutrals with low proton affinities, notably those with the radical X groups $CH_2^{\cdot}$ and $O^{\cdot}$, have singularly large values of $\delta PA(X)$. Other X groups lie comfortably in between for both proton affinities and the difference quantity of interest. Linear regression analysis allows us to quantitate this observation. For all of the bases discussed in this article, we derive the following equation:

$$\begin{aligned}\delta PA(X) &\equiv [PA(C_6H_5X) - PA(C_2H_3X)]\\ &= -0.3735(\pm 0.0664)PA(C_2H_3X)\\ &\quad + 347.0(\pm 16.2) \qquad (r^2 = 0.742)\end{aligned} \tag{3}$$

whereas if the radical X groups $O^{\cdot}$ and $CH_2^{\cdot}$ are omitted, we obtain the negligibly more accurate equation

$$\begin{aligned}\delta PA(X) &\equiv [PA(C_6H_5X) - PA(C_2H_3X)]\\ &= -0.2484(\pm 0.0474)PA(C_2H_3X)\\ &\quad + 235.0(\pm 9.5) \qquad (r^2 = 0.753)\end{aligned} \tag{4}$$

Fig. 1 pictorially presents both Eqs. (3) and (4). These equations may be recast as

$$PA(C_6H_5X) = 0.626PA(C_2H_3X) + 347.0 \tag{5}$$

$$PA(C_6H_5X) = 0.752PA(C_2H_3X) + 235.0 \tag{6}$$

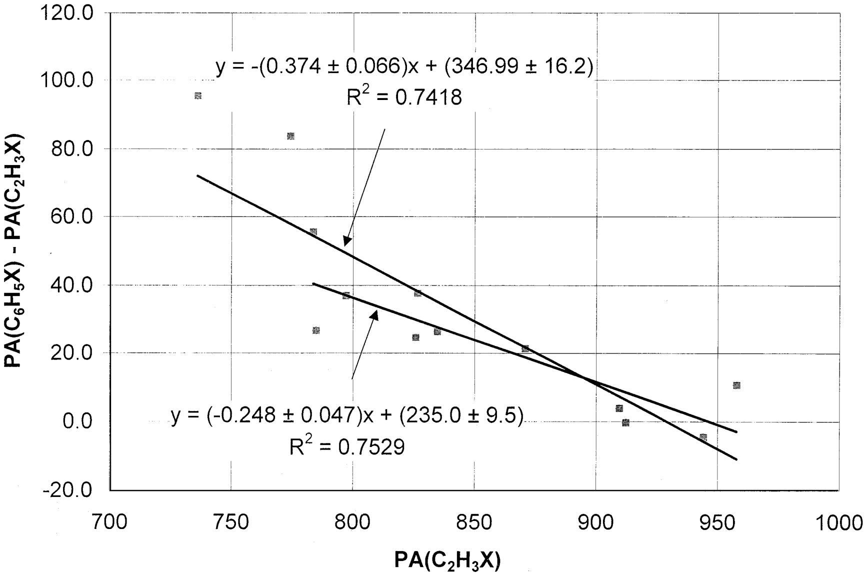

Fig. 1. Linear regression lines for PA(C_6H_5X) − PA(C_2H_3X vs. PA(C_2H_3X) where the two lines are for the cases with and without $X = CH_2^{\cdot}$ and $O^{\cdot}$, Eqs. (3) and (4).

Expressed in this latter way it is seen that the effect of the group X on the proton affinity of the phenyl species is less than that on the vinyl species (i.e. the above phenyl versus vinyl slopes are less than unity). This finding is initially surprising: the polarizability of ethylene is less than that of benzene and so we expect substituent effects to be smaller for the former than the latter. That the proton affinities of the various phenyl species are almost always larger than the corresponding vinyl compound does, however, affirm the traditional understanding.

We recall the now standard analyses of substituent effects on ionic reactions: the names Hammett, Taft, Swain, and Topsom come immediately to mind. However important in our discipline, these approaches are not relevant here. They assume a constant basic or acidic site and we are looking at variously substituted species containing this site. For example, we might wish to compare the proton affinities of a set of substituted benzaldimines, i.e. *m*- and *p*-XC_6H_4CHNH where X includes the groups presented in Table 1 except for those that are more basic than the CHNH functionality, and so are protonated on the "wrong site," much as we earlier eliminated X = F, Cl, and Br because their phenyl- and vinyl-containing species are protonated on one of the carbons instead of the X atom [5].

Finally, we note that our entire study can be recast in terms of the putative thermoneutrality for the isodesmic reactions

$$C_2H_3X + C_6H_5Y \rightarrow C_2H_3Y + C_6H_5X \tag{7}$$

$$C_2H_3XH^+ + C_6H_5YH^+ \rightarrow C_2H_3YH^+ + C_6H_5XH^+ \tag{8}$$

$$C_2H_3X + C_6H_5XH^+ \rightarrow C_2H_3XH^+ + C_6H_5X \tag{9}$$

$$C_2H_3X + C_6H_5YH^+ \rightarrow C_2H_3Y + C_6H_5XH^+ \tag{10}$$

[1] documents that Eq. (7) is quite thermoneutral (i.e. within 10 kJ mol^{-1}) for a wide variety of X and Y. Admittedly, not all of the substituents in the current study have been so affirmed—we are missing enthalpies of formation of numerous vinyl and/or phenyl species. We are optimistic that Eq. (7) is generally true and so, following the lead of [1], could reliably use this equation to predict the missing values. Our study shows that Eqs. (8)–(10) are not thermoneutral. It has long been known that additivity rules are much

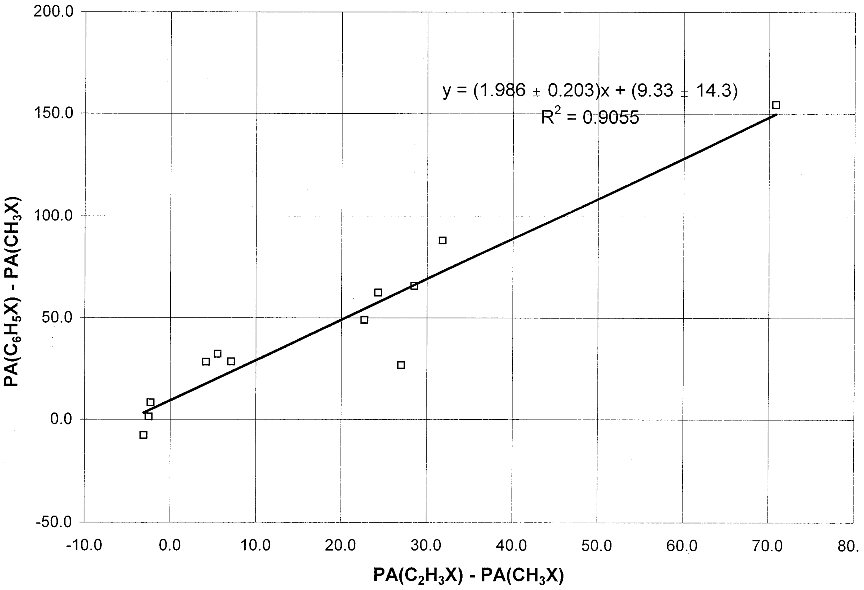

Fig. 2. Linear regression line for PA(C_6H_5X) − PA(CH_3X) vs. PA(C_2H_3X) − PA(CH_3X), Eq. (15), where $X = CH_2^{:}$ has been omitted for reasons given elsewhere in the text.

less reliable within the province of ion energetics than that of the thermochemistry of neutrals and so we are not particularly surprised, but merely disappointed. What remains surprising is that a simple interpretation is evasive.

Furthermore, in principle, isodesmic reactions can be used to deduce stabilization of substituted compounds relative to simpler species, say the methyl or even hydrogen derivatives. Consider now the following isodesmic reactions

$$CH_3X + C_6H_5Y \rightarrow CH_3Y + C_6H_5X \tag{11}$$

$$CH_3X + C_2H_3Y \rightarrow CH_3Y + C_2H_3X \tag{12}$$

$$HX + C_6H_5Y \rightarrow HY + C_6H_5X \tag{13}$$

$$HX + C_2H_3Y \rightarrow HY + C_2H_3X \tag{14}$$

From the above it is clear we cannot investigate the enthalpies of formation of the totality of either neutral phenyl and vinyl species nor their protonated analogs. Proton affinities, however, are amenable to this type of analysis. Even better, we can take a composite of our earlier phenyl/vinyl comparison and linear regression analysis by considering phenyl-methyl/vinyl-methyl and phenyl-hydrogen/vinyl-hydrogen comparisons [6] from which we derive

$$\begin{aligned} \mathrm{PA}(C_6H_5X) - \mathrm{PA}(CH_3X) &= (1.986 \pm 0.203)[\mathrm{PA}(C_2H_3X) \\ &\quad - \mathrm{PA}(CH_3X)] + 9.33(\pm 14.3) \\ &\quad (r^2 = 0.906) \end{aligned} \tag{15}$$

$$\begin{aligned} \mathrm{PA}(C_6H_5X) - \mathrm{PA}(HX) &= (1.479 \pm 0.064)[\mathrm{PA}(C_2H_3X) \\ &\quad - \mathrm{PA}(HX)] + 3.12(\pm 10.3) \\ &\quad (r^2 = 0.981) \end{aligned} \tag{16}$$

Figs. 2 and 3 pictorially present Eqs. (15) and (16), respectively. The intercepts are statistically equal to zero: the slopes are very different from unity. Had these idealized zero and unity values been found, we would have immediately derived, and so affirmed, Eq. (2). Instead we have a conceptually more compli-

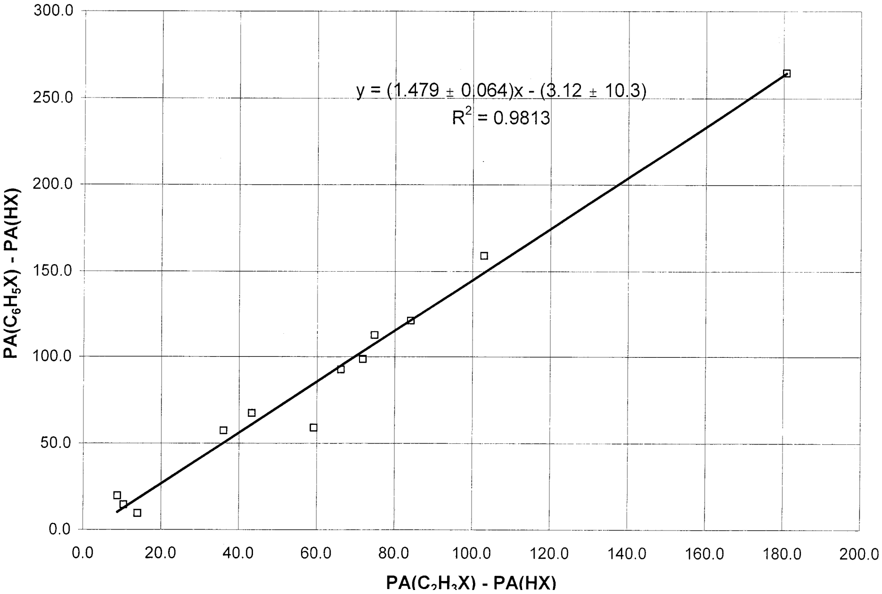

Fig. 3. Linear regression line for PA(C_6H_5X) − PA(HX) vs. PA(C_2H_3X) − PA(HX), Eq. (16), where $X = CH_2^{\cdot}$ has been omitted for reasons given elsewhere in the text.

cated, but empirically more accurate, relation connecting the thermochemistry of phenyl and vinyl derivatives.

3. Conclusions and reiteration

Returning now to the experimentally measured examples in Table 1, it is seen that the conjugating power of the various X and XH^+ vary. The X seem generally quite innocuous and so the difference of their effects with vinyl and phenyl groups is expected to be small, i.e. $\delta H(X)$ for neutral X is very nearly constant. However, many of the XH^+ are expected to have much stronger conjugating power as well as more powerful polarizing power than neutral groups X. Perhaps, it is not so strange that δPA(X) [and hence the value of $\delta H(XH^+)$] is not particularly independent of X and its charged counterparts.

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References

[1] (a) J.F. Liebman, in Molecular Structure and Energetics: Studies of Organic Molecules, J.F. Liebman, A. Greenberg (Eds.), VCH, Deerfield Beach, 1986, p. 267; (b) P. George, C.W. Bock, M. Trachtman, in Molecular Structure and Energetics: Biophysical Aspects, J.F. Liebman, A. Greenberg (Eds.), VCH, New York, 1987, p. 163; (c) Y.-R. Luo, J.L. Holmes, J. Phys. Chem. 96 (1992) 568; (d) Y.-R. Luo, J.L. Holmes, J. Phys. Org. Chem. 7 (1994) 403.

[2] S.W. Benson, Chem. Rev. 78 (1978) 23.

[3] See, for example, (a) S.W. Slayden, J.F. Liebman, W.G. Mallard, in The Chemistry of Functional Groups, Supplement D2: The Chemistry of Organic Halides, Pseudohalides and Azides, S. Patai, Z. Rappoport (Eds.), Wiley, Chichester, UK, 1995, p. 361; (b) J.F. Liebman, H. Afeefy, Thermodynamical Modeling and Materials Data Engineering, J.-P. Caliste, E. Truyol, J. Westbrook (Eds.), Springer, to be published.

[4] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data, to be published.

[5] In fact, we welcome such a study because it remains equivocal whether the parent neutral species and the derived protonated ion, indeed have these structures C_6H_5CHNH, and the derived protonated ion, $C_6H_5CHNH_2^+$, as opposed to troponimine, C_7H_6NH and aminotropylium ion, $C_7H_6NH_2^+$, respectively; cf.

R.A.L. Peerboom, S. Ingemann, N.M.M. Nibbering, J.F. Liebman, J. Chem. Soc. Perkin Trans. 2 (1990) 1825.

[6] We explicitly leave out the substituent $CH_2^{\cdot}$ because its derivatives are not comparable. That is, its protonated phenyl and vinyl derivatives are ionized toluene and propene, i.e. π-ionized species with classical C–H bonds. By contrast, its protonated methyl and hydrogen species are ionized ethane and methane, i.e. σ-ionized species with 1-electron C–H bonds. By contrast, we include the substituent $O^{\cdot}$ because all of its protonated species may be understood as the radical cation formed by formal loss of an oxygen lone pair electron from some hydroxylic (ROH: phenol, enol, alcohol, water) species.