J. Org. Chem. 1991, 56, 1615-1622

Some Properties and Trends of Enthalpies of Vaporization and of Trouton's Ratios of Organic Compounds. Correlation of Enthalpies of Vaporization and of Enthalpies of Formation with Normal Boiling Points

Constantinos G. Screttas* and Maria Micha-Screttas

Institute of Organic Chemistry, The National Hellenic Research Foundation, Athens 116 35, Greece

Received November 6, 1989 (Revised Manuscript Received March 9, 1990)

Enthalpies of vaporization of homologous series *n*-RY (Y = H, Cl, Br, I, OH, SH, NH_2, CN, COOH, OAc, and COOMe) or *n*-R^1YR^2-*n* (Y = O, S, NH, CO) have been correlated with the respective carbon numbers or sums of carbon numbers. These correlations imply that enthalpies of vaporization of any two series are linearly related to each other. Other important implications of these correlations are (a) from the stand point of thermochemistry the fundamental unit of a normal alkyl is a methylene group and (b) the contribution to the enthalpy of vaporization of an alkyl group is transferable and additive. Enthalpies of vaporization of sequences of compounds with normal alkyls plot linearly against the respective enthalpies of formation. Branched alkyls are in all cases below the regression line. This is taken to be a thermochemical manifestation of the steric effect of branched alkyl groups. A set of steric substituent constants of branched alkyls from C_3 to C_5 has been derived from thermochemical data. Enthalpies of vaporization of sequences of compounds which belong to the same class, e.g. halides, are shown to be linearly related to the respective normal boiling points. A number of correlations between enthalpies of formation and normal boiling points are also reported. Trouton's ratios of homologous series of compounds *n*-RY or *n*-R^1YR^2-*n* are correlated with the respective carbon numbers or sums of carbon numbers. A method is proposed for estimating normal boiling points of high-boiling organic compounds with normal alkyl chains.

There are a number of important phenomena in organic chemistry which depend upon the liquid state. For example, we could mention the dependence of the rate or direction of certain organic reactions on the solvent medium, the so-called solvent effect, the influence of the solvent on the degree of association of an organic solute, the medium dependent response to the electromagnetic radiation, i.e. solvatochromism, etc. These and many other relevant phenomena are certainly important for understanding organic reactivity in condensed phases. A thermochemical parameter which reflects the "structure" of a liquid is the enthalpy of vaporization. Indeed, enthalpies of vaporization depend upon the strength of the intermolecular forces. For example, the occurrence or not of hydrogen bonding could be inferred from "anomalies" observed in the enthalpies of vaporization of a sequence of constitutionally analogous compounds, e.g. alcohols versus thiols.[1] If we now consider a reaction that takes place in solution, it can be readily envisaged that at the early stages of the transition state the reactants are brought together by the same forces which are responsible for the enthalpy of vaporization. Therefore, it becomes apparent that an examination of the enthalpies of vaporization from the standpoint of organic structure and reactivity could be fruitful. Already the success of various methods for predicting enthalpies of vaporization[2-4] indicates that a relation between structure and enthalpy of vaporization does exist. However, relatively little has been done in the direction of correlating thermochemical parameters with other molecular parameters. Reaction exothermicities are linearly related to activation energies of free radical reactions through the well known Evans-Polanyi (E-P) relationship.[5] Other variants of the E-P correlations involve homolytic bond dissociation energies of the bond that is being broken[6] or formed.[7] Likewise, heterolytic bond dissociation energies have been correlated with activation energies of gas-phase decomposition reactions.[8] Exothermicities for hydrogen abstraction by an iodine atom for a series of hydrocarbons have been used as additive substituent constants in a correlation involving ionization potentials of dialkyl ketones.[8] The ratio of the enthalpy of vaporization at the normal boiling point and the normal boiling point in Kelvin is supposed to be a constant for all non-hydrogen bonded liquids. This is the so-called Trouton's rule. Of course, the constancy of the ratio is the exception rather than the rule.[9] Recently, we reported a number of correlations between enthalpies of formation and ionization potentials of certain atoms or free radicals.[10] It is of particular relevance to mention a correlation between enthalpies of vaporization and a solvent polarity parameter.[2] The purpose of this work is to point out some trends in enthalpies of vaporization and/or Trouton's ratios, to report certain correlations between the latter parameters and other molecular parameters, and finally to discuss the implications of these correlations.

Interrelation of ΔH_v and/or ΔH_f's. Perhaps the most common trend among thermochemical data in general is the linear dependence of the thermochemical parameter of a homologous series of organic compounds with *normal alkyl chains* on the carbon number *n*.[11] This holds true for enthalpies of vaporization as well.[12] It has been noted[13] that hydrocarbons of diverse structure which have equal carbon numbers exhibit approximately equal enthalpies of vaporization. In fact it was shown that enthalpies of

---

[1] Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; Chapter 12.

[2] Chickos, J. S.; Hesse, D. G.; Liebman, J. F.; Panshin, S. Y. *J. Org. Chem.* **1988**, *53*, 3424.

[3] Guthrie, J. P.; Taylor, K. F. *Can. J. Chem.* **1983**, *61*, 602. DuCros, M.; Greison, J. F.; Sannier, H. *Thermochim. Acta* **1980**, *36*, 39.

[4] Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1989**, *54*, 5250.

[5] See, for example: O'Neal, H. E.; Benson, S. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 275.

[6] Trotman-Dickenson, A. F. *Chem. Ind. (London)* **1965**, 379. Cadman, P.; Dodwell, C.; White, A. J.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1971**, 2967.

[7] Screttas, C. G. *J. Org. Chem.* **1980**, *45*, 1620.

[8] Screttas, C. G. *J. Org. Chem.* **1980**, *45*, 333.

[9] See, for example: Hildebrand, J. H. *J. Chem. Soc., Faraday Disc.* **1978**, 66.

[10] Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1989**, *54*, 5132.

[11] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970; p 518.

[12] Mannson, M.; Sellers, P.; Stridh, G.; Sunner, S. *J. Chem. Thermodyn.* **1977**, *9*, 91.

[13] Chickos, J. D.; Hyman, A. S.; Ladon, L. H.; Liebman, J. F. *J. Org. Chem.* **1981**, *46*, 4294.

0022-3263/91/1956-1615$02.50/0

Table I. Regression Equations of the ΔH°_v vs n (or Σn) Correlations[a]

sequence	regression equation	r	range of n	sequence	regression equation	r	range of n
n-RH	ΔH°_v (kJ M^{-1}) = $5.018n + 1.1336$	0.9998	2, 3, 5–12	n-R^1SR^2-n	ΔH°_v (kJ M^{-1}) = $4.190\Sigma n + 19.433$	0.9990	2, 3, 4, 4, 5, 5, 6, 6, 6, 8
n-$RCH{=}CH_2$	ΔH°_v (kJ M^{-1}) = $4.951n + 10.973$	0.9999	1, 2, 6, 8, 10, 14	n-RNH_2	ΔH°_v (kJ M^{-1}) = $4.368n + 18.804$	0.9983	1, 3–7
n-RPh	ΔH°_v (kJ M^{-1}) = $4.391n + 33.505$	0.9984	1–4	n-R_2NH	ΔH°_v (kJ M^{-1}) = $4.036\Sigma n + 16.440$	0.9954	2, 4, 6, 8
n-RCl	ΔH°_v (kJ M^{-1}) = $4.824n + 14.043$	0.9998	3–7, 12, 16	n-R_3N	ΔH°_v (kJ M^{-1}) = $3.998\Sigma n + 10.447$	–	3, 6, 9
n-RBr	ΔH°_v (kJ M^{-1}) = $4.739n + 17.985$	0.9997	1–8, 12, 16	n-RCN	ΔH°_v (kJ M^{-1}) = $4.433n + 26.863$	0.9984	1–11, 13
n-RI	ΔH°_v (kJ M^{-1}) = $4.437n + 23.066$	0.9998	2–6	n-R^1COR^2-n	ΔH°_v (kJ M^{-1}) = $4.574\Sigma n + 20.650$	0.9980	2–4, 5, 5, 6, 8, 10, 11
n-ROH	ΔH°_v (kJ M^{-1}) = $4.934n + 32.461$	0.9997	1–10, 12, 14	n-RCOOH	ΔH°_v (kJ M^{-1}) = $3.200n + 48.467$		1–3
n-RSH	ΔH°_v (kJ M^{-1}) = $4.759n + 17.760$	0.9999	2–5, 10	n-ROAc	ΔH°_v (kJ M^{-1}) = $3.825n + 28.400$	0.9982	1–4
n-R^1OR^2-n	ΔH°_v (kJ M^{-1}) = $4.710\Sigma n + 8.582$	0.9971	2, 4, 4, 5, 5, 6, 6, 6, 7, 7, 7, 8, 8, 9, 9, 10, 10	n-RCOOMe	ΔH°_v (kJ M^{-1}) = $4.726n + 25.086$	0.9975	1–14

[a] Data from ref 11, see statement for supplementary material.

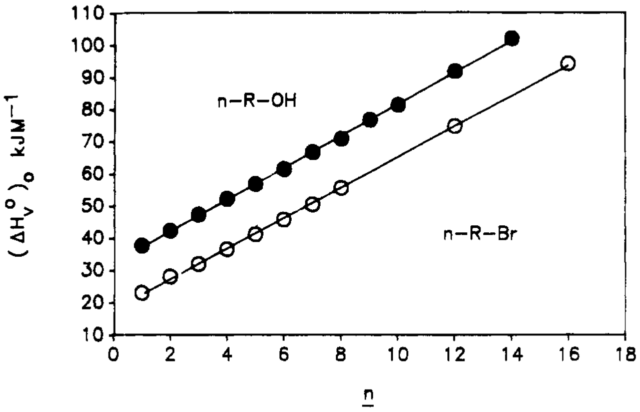

Figure 1. Standard enthalpies of vaporization at 298.15 K for 1-alkanols and of n-alkyl bromides (from ref 14) plotted against the respective carbon numbers.

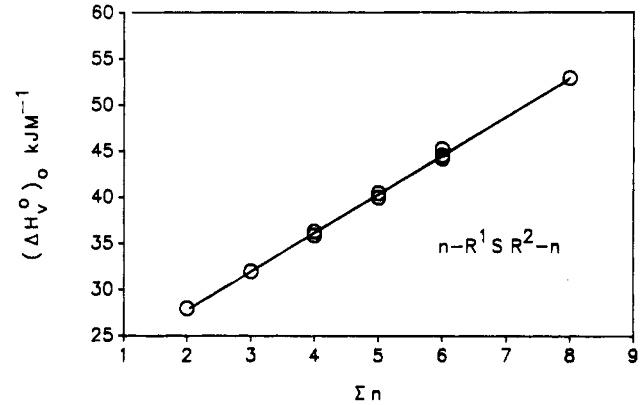

Figure 2. Standard enthalpies of vaporization at 298.15 K of di-n-alkyl sulfides (from ref 14) plotted against the corresponding sum of carbon numbers.

vaporization of hydrocarbons plot reasonably linear against the respective carbon numbers.[13] Figure 1 shows a plot of the enthalpies of vaporization for the homologous series of n-RBr and n-ROH against the respective carbon numbers. Figure 2 is a plot of the enthalpies of vaporization of thioethers[14] n-R^1S-R^2-n, against the respective *sums* of carbon numbers which correspond to the two alkyls. In this case two or more different thioethers could have equal sums of carbon numbers but different enthalpies of vaporization. For example, the points for Et_2S and n-PrSMe correspond to a sum of carbon numbers equal to 4. Likewise, n-Pr_2S, n-BuSEt, and n-$C_5H_{11}SMe$ correspond to a sum of carbon numbers equal to 6. Although the correlation in Figure 2 seems to be obeyed, if one examines the data more carefully one can observe a "fine structure". Namely, the lowest enthalpy of vaporization is exhibited by the symmetric compound, i.e., the one for which n-R^1 = R^2-n. As the difference of the carbon numbers n^1 and n^2 increases the enthalpy of vaporization increases likewise. Thus the enthalpy of vaporization[14] of n-Pr_2S, n-BuSEt, and n-$C_5H_{11}SMe$ is respectively 44.23, 44.53, and 45.25 kJ/mol. Although the differences are within the limits of the experimental error, it is felt that the above statement is justified to a considerable extent by the observed analogous trend in ethers and secondary amines. Namely, n-Pr_2O, 35.79; n-BuOEt, 36.41; n-$C_5H_{11}OMe$, 36.91 kJ/mol;[14] n-Bu_2NH, 49.47; and n-$C_5H_{13}NHEt$, 52.22 kJ/mol.[14]

Table I summarizes the regression equations which correspond to plots of standard enthalpies of vaporization at 298.15 K versus carbon numbers or sums of carbon numbers for various classes of organic compounds. It should be pointed out that in certain cases there is more than one way of plotting enthalpies of vaporization against carbon numbers. For example, the data for normal 1-alkenes, n-$RCH{=}CH_2$, plot linearly against the carbon number corresponding to the n-R group of n-$RCH{=}CH_2$ as well as against the total carbon number, i.e., $n + 2$. Similarly, the data for n-RPh plot linearly both against n or $n + 6$. These two alternative plots exhibit identical slopes, but they have markedly different intercepts. In order to decide which type of plot is more meaningful we have to examine the implications of the observed linearity. We believe that the linearity implies an *equal distribution of energy among the molecular subunit corresponding to the carbon numbers.* The first type of plot implies that every carbon unit, or to be more exact, every methylene group, accommodates an equal amount of energy of that residing in the n-R moiety of the n-$RCH{=}CH_2$ molecule. The second type of plot implies that all types of molecular subunits, i.e., $-CH_2-$, $-CH{=}$, and $CH_2{=}$, accommodate and equal amount of energy. One can decide that the former type of plot could be more meaningful on the basis of the following reasoning. Bader et al.[15] showed theoretically that in the series of normal hydrocarbons all methylene groups,

---

(14) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds*; Blackwell Scientific Publications: Oxford, 1985.

(15) Bader, R. F. W.; Carroll, M. T.; Cheesman, J. R.; Chang, C. *J. Am. Chem. Soc.* 1987, *109*, 7968.

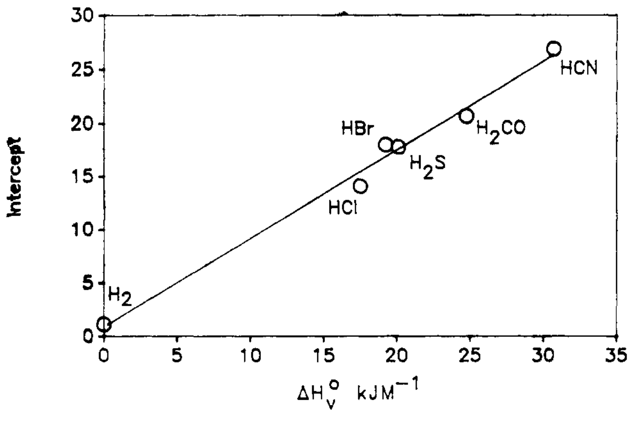

Figure 3. The intercepts of the ΔH°_v vs n or Σn regression equations (from Table I) for n-RH, n-RCl, n-RBr, n-RSH, n-R_2CO, and n-RCN plotted against the enthalpy of vaporization at the boiling point (from ref 16) of H_2, HCl, HBr, H_2S, H_2CO, and HCN, respectively.

regardless of their relative position in the normal carbon chain, possess equal volumes and equal energies. For example, although the 2- and 3-methylene groups in the n-pentane are not identically substituted, namely "methyl-n-propylmethane" versus "diethylmethane", they still have identical properties, or in other words, they contribute by a constant amount to the "molar" property of the hydrocarbon. This effect constitutes the phenomenon of *transferability* and *additivity*. In addition, the success of the bond or group additivity methods[3] for estimating enthalpies of vaporization suggests rather strongly that only identical molecular subunits could have equal contributions. But since the point for $n = 1$ is on the regression line of the ΔH°_v vs n correlation we are forced to consider compounds such as n-RCH=CH_2 or n-RY as $H(CH_2)_nCH{=}CH_2$ or $H(CH_2)_nY$. This then helps us assign a physical meaning to the constants of the linear regression equations of ΔH°_v vs n or Σn plots. Thus the slope can be identified with the methylene group contribution to the "molar" enthalpy of vaporization, whereas the intercept to the enthalpy of vaporization of the "parent" compound, HCH=CH_2, or HY, in the case of the latter two examples. The constancy of the methylene group contribution to the enthalpy of vaporization within a series of n-RY implies that from the standpoint of thermochemistry *the fundamental unit of a normal alkyl chain is a methylene group*. The identification of the intercept of the ΔH°_v versus n straight line with the enthalpy of vaporization of the parent compound, HY, seems to be very nearly justified. For example, for the data of n-RPh the intercept is 33.50 kJ/mol, and this should be compared to the enthalpy of vaporization of benzene, i.e., 33.92 kJ/mol.[14] Similarly, for the series of hydrocarbons the intercept is equal to 1.13 kJ/mol, versus the value 0.00 kJ/mol for the enthalpy of vaporization of H_2 at 298 °C, i.e., above its critical temperature. In fact if one plots the intercepts of the regression lines of n-RH, n-RCl, n-RBr, n-RSH, n-R^1COR^2-n, and n-RCN against the enthalpy of vaporization[16] of H_2, HCl, HBr, H_2S, H_2CO, and HCN, one obtains Figure 3. The plot is reasonably linear with a slope of 0.89.[17] One could attribute some significance to the correlation in Figure 3. Namely, it could be taken as a thermochemical link between organic and inorganic chemistry. A specific comment is in order regarding the intercept of the regression line for the normal hydrocarbons, i.e. 1.13 kJ/mol. This value is markedly different from the value of ca. 3.0 kJ/mol which has been reported by Chickos et al.[13] The latter authors noticed that the intercept is approximately equal to RT when T is ca. 300 K. In the correlation of Chickos et al.[13] were included hydrocarbons of diverse structure. For example, octanes, octenes, and octynes, all with $n = 8$, were included in the same correlation, although the enthalpy of vaporization of these compounds exhibits a range of 4.0 kJ/mol. It appears reasonable to believe that the higher value of the intercept in the plot that included hydrocarbons of various structure[13] is due to the numeric analytical treatment of these data which exhibit a correlation coefficient 0.965 versus 0.9998 for the n-RH data.

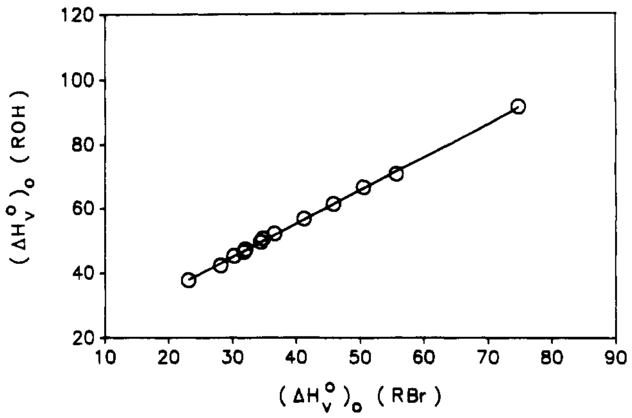

Figure 4. Standard enthalpies of vaporization at 298.15 K of alkanols plotted against the respective of alkyl bromides (data from ref 14).

An examination of the data in Table I leads to the following conclusion: The normal hydrocarbons exhibit the largest methylene group contribution to the enthalpy of vaporization, ca. 5.02 kJ/mol (4.184 kJ = 1.0 kcal). The corresponding values for the series of n-RCH=CH_2 and n-RPh are 4.95 and 4.39 kJ per methylene group, respectively. In the series n-RCl, n-RBr, and n-RI, the methylene group contribution decreases with decreasing electronegativity of the halogen. The same is true for the n-ROH and n-RSH or n-R_2O and n-R_2S series. In the series of n-RNH_2, n-R_2NH, and n-R_3N, the methylene group contribution decreases in the same order. Here the intercepts of the respective regression lines deserve some discussion. We notice that the intercept decreases from the primary through the secondary to tertiary amines. This can be understood on the basis that the intercept of n-R_3N case corresponds to the enthalpy of vaporization of NH_3 in the absence of hydrogen bonding (i.e., "ideal" ammonia), whereas, in n-R_2NH and n-RNH_2 the respective intercepts correspond roughly to $^2/_3$ and $^1/_3$, respectively, of the "ideal" enthalpy of vaporization of NH_3 increased by the energy due to hydrogen bonding.

The ΔH°_v versus n correlation implies that *any two series of enthalpies of vaporization are linearly related to each other*, e.g. Figure 4, where enthalpies of vaporization of alkanols are plotted against the respective data of alkyl bromides. What is of importance, however, is the fact that in the plot are also included the data for branched alkyl derivatives which seem to comply with the correlation holding for the normal chain compounds. Enthalpies of vaporization of a series of organic compounds when plotted against the respective enthalpies of formation,[18] e.g. Figures

---

[16] *Handbook of Chemistry and Physics*, 54th ed. 1973-74, CRC Press: Boca Raton, FL, 1973-74; pp D-162, D-182.

[17] The "estimated" enthalpies of vaporization, i.e., the intercepts of the regression equations, and the experimental enthalpies of vaporization of the parent compounds are not at the same conditions. The former are derived from standard enthalpies of vaporization at 298.15 K, whereas the latter (ref 16) have been derived from vapor pressure-temperature data and the Clapeyron equation, and they are valid within certain temperature limits, including the normal boiling point (see ref 14, p 27).

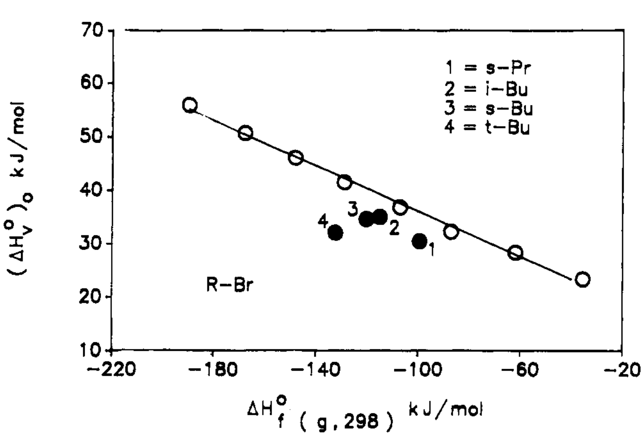

Figure 5. Standard enthalpies of vaporization at 298.15 K (from ref 14) of alkyl bromides plotted against the respective enthalpies of formation (*g*, 298.15 K) (from ref 18).

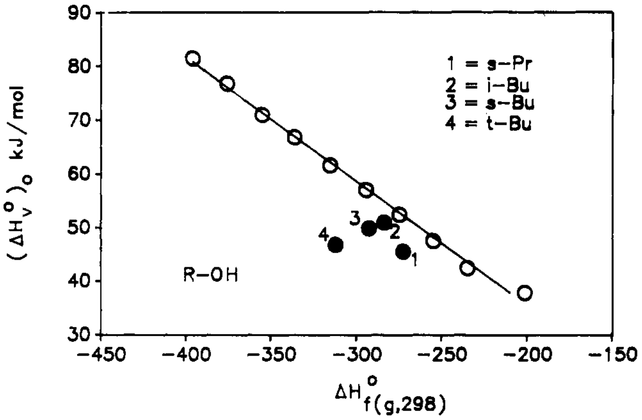

Figure 6. Standard enthalpies of vaporization at 298.15 K of alkanols plotted as in Figure 5 (data from refs 14, 18).

5–6, for RBr and ROH, respectively, indicate that they correlate only for R = a normal alkyl. The points corresponding to the branched alkyl compounds, i.e., *s*-Pr, *i*-Bu, *s*-Bu, and *t*-Bu, are below the regression line. It is felt that this phenomenon provides a thermochemical manifestation of the steric effect of the branched alkyls. We attribute this phenomenon to the markedly different fraction of energy in enthalpies of vaporization and of formation which is due to nonbonded interactions. The latter according to Pitzer and Catalano[19] arise from London forces. Indeed, it appears reasonable to believe that steric factors are involved in nonbonded interactions between C–H bonds, hence the lower dispersion energies involved with branched alkyl compounds as compared to the respective isomeric ones with normal alkyl chains. It is worth noting that in both cases, Figures 5 and 6, the deviating points follow a similar pattern, namely, the deviation along the *Y* axis from the regression line in both cases is *t*-Bu > *s*-Bu = *s*-Pr > *i*-Bu. The regression equations of the straight lines in Figures 5 and 6 are given by eqs 1–2, respectively.

$$\Delta H^o_v(n\text{-RBr}) = -0.212\Delta H^o_f(n\text{-RBr}) + 14.730 \quad (1)$$

$$\Delta H^o_v(n\text{-ROH}) = -0.231\Delta H^o_f(n\text{-ROH}) - 10.729 \quad (2)$$

The deviations along the *Y* axis of the branched alkyls, which we denote as $\Delta\Delta H_{vf}$, are calculated as follows: We introduce the enthalpy of *formation* of the branched alkyl into the appropriate regression equation and we obtain a calculated value, $(\Delta H^o_v)_{calc}$, for the branched alkyl. For the latter value we subtract the experimental enthalpy of *vaporization*, ΔH^o_v, and this difference constitutes the deviation along the *Y* axis of the point in question. For example, the deviation of the point of *t*-BuOH is given by eq 3. Now if we plot the $\Delta\Delta H_{vf}$ values of branched alcohols against the respective values of the branched alkyl bromides we obtain Figure 7, which is reasonably linear. This means that the values $\Delta\Delta H_{vf}$ are transferable. Therefore, we can calculate a set of $\Delta\Delta H_{vf}$ values derived from any series of compounds, e.g. alkanols, and use them as steric substituent constands. Table II summarizes such a set for the C_3 up to C_5 branched alkyls. An inspection of the data in Table I shows a marked internal consistency. Namely, iso-type alkyls exhibit a value ranging from 3.2 to 3.9 kJ/mol. Alkyl groups of the sec-type range from 6.7 to 9.2, the upper limit exhibited by those that have additional branching, e.g. *s*-Pr(Me)CH. Lastly, the tert-type substituents have a value around 15 kJ/mol.

$$\begin{aligned}\Delta\Delta H_{vf} &= (\Delta H^o_v)_{calc}(t\text{-BuOH}) - \Delta H^o_v(t\text{-BuOH}) = \\ &-0.231\Delta H^o_f(t\text{-BuOH}) - 10.729 - \Delta H^o_v(t\text{-BuOH}) = \\ &-0.231(-312.5) - 10.729 - 46.74 = 14.71\ \text{kJ/mol} \quad (3)\end{aligned}$$

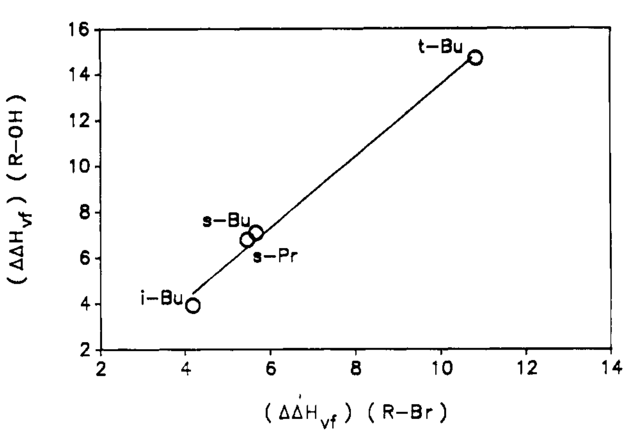

Figure 7. The deviations (along the *Y* axis) of the branched alkyls from the regression (ΔH^o_v vs ΔH^o_f) line of alkanols plotted against the respective deviations of the alkyl bromides.

Table II. Proposed Steric Substituent Constants of Certain C_3–C_5 Branched Alkyls Derived from $\Delta\Delta H_{vf}$ Values of Alkanols

substituent	steric constant[a]	substituent	steric constant[a]
n-R	0.00	*s*-Bu	7.61
i-BuCH$_2$	3.24	Et$_2$CH	8.12
s-BuCH$_2$	3.85	*s*-Pr(Me)CH	9.17
i-Bu	3.89	*t*-Bu	14.71
s-Pr	6.74	Et(Me)$_2$C	15.52
n-Pr(Me)CH	7.53		

[a] The indicated values are absolute values in kilojoules per mole.

Enthalpies of Vaporization and Boiling Points. It has already been mentioned that Trouton's rule, i.e., the ratio of the enthalpy of vaporization at the normal boiling point and the normal boiling point in Kelvin, is only obeyed by a few low molecular weight non-hydrogen bonded liquids. We have observed that either the standard enthalpies of vaporization at 298.15 K or the enthalpies of vaporization at the normal boiling point of sequences of compounds that belong to the same class plot linearly against the respective normal boiling points. This can be examplified by the plot in Figure 8, where the standard enthalpies of vaporization at 298.15 K of alkyl halides are

---

(18) Lias, L. S.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(19) Pitzer, K. S.; Catalano, E. *J. Am. Chem. Soc.* **1956**, *78*, 4844.

Table III. Regression Equations of ΔH°_v (kJ/mol) vs T_b (K) Correlations and Relevant Data

sequence	regression equation	r	n	range (in T_b)
RX	$\Delta H^\circ_v = 0.145T_b - 17.587$	0.994	31	276-431
RSH, R_2S	$\Delta H^\circ_v = 0.151T_b - 19.611$	0.993	35	308-443
RCHO, R_2CO	$\Delta H^\circ_v = 0.154T_b - 19.468$	0.995	19	293-401
RNH_2, R_2NH, R_3N	$\Delta H^\circ_v = 0.160T_b - 20.885$	0.988	24	266-433
R_2O	$\Delta H^\circ_v = 0.166T_b - 24.576$	0.994	47	303-427
RCN	$\Delta H^\circ_v = 0.170T_b - 26.725$	0.975	14	354-423
ROH	$\Delta H^\circ_v = 0.210T_b - 28.693$	0.991	16	370-431
RCOOR′	$\Delta H^\circ_v = 0.159T_b - 20.196$	0.992	25	304-423
c-alkanes, alkylcycloalkanes, bicyclics	$\Delta H^\circ_v = 0.134T_b - 14.408$	0.999	18	240-405
RPh	$\Delta H^\circ_v = 0.175T_b - 29.681$	0.995	16	383-509

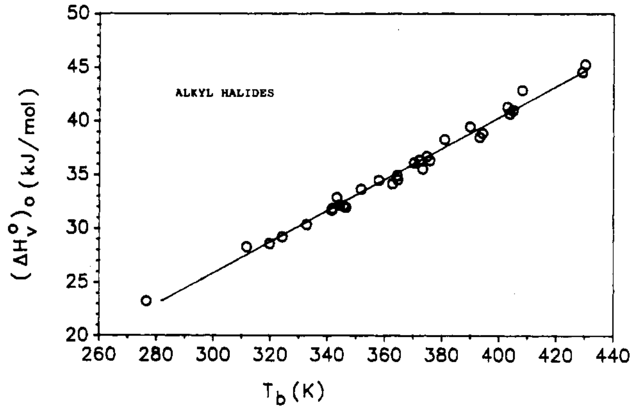

Figure 8. Standard enthalpies of vaporization at 298.15 K of alkyl halides plotted against the respective normal boiling points (data from ref 14).

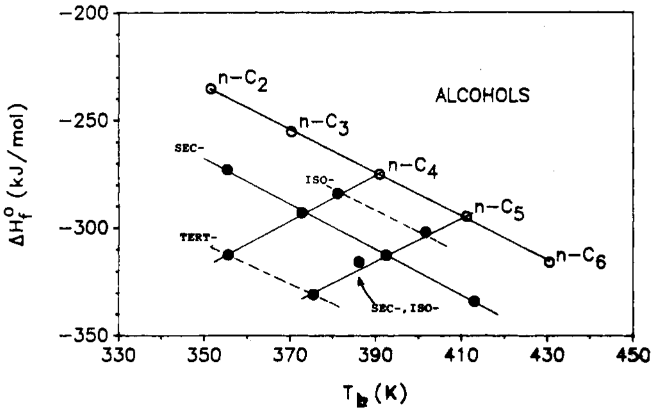

Figure 9. Standard enthalpies of formation (g, 298.15 K) of C_2 to C_6 alkanols plotted against the corresponding normal boiling points (enthalpies of formation from ref 18, boiling points from ref 16).

plotted against the respective normal boiling points in Kelvin. The regression equation corresponding to the straight line in Figure 8 is given by eq 4. It is worth noting

$$\Delta H^\circ_v \text{ (kJ/mol)} = 0.145T_b - 17.587 \ (n = 31, r = 0.994) \quad (4)$$

that in Figure 8 are included data for fluorides, chlorides, bromides, and iodides, primary, secondary, and tertiary ones, as well as monohalobenzenes. Heptyl halides and the higher ones exhibit a marked, positive deviation from the regression line of Figure 8, i.e., 2 kJ/mol or higher. The regression equations corresponding to plots like Figure 8 for various classes of organic compounds are summarized in Table III. These regression equations enable one to obtain an estimate of the enthalpy of vaporization of a compound whose the normal boiling point is known, provided that it is within the appropriate limits for which the regression equation is valid. The standard enthalpies of vaporization at 298.15 K of hydrocarbons in general cluster around a strait line whose the regression equation is given by (5). However, a closer examination of the data shows

$$\Delta H^\circ_v = 0.151T_b - 19.735 \ (n = 58, r = 0.989) \quad (5)$$

the following: (1) ΔH°_v vs T_b relationship for the saturated hydrocarbons exhibits a shallow concavity. (2) Cycloalkanes, alkylcycloalkanes, and bicyclic hydrocarbons comply with eq 6. (3) The data for alkylbenzenes are expressed by eq 7. It can be seen that the plots of the

$$\Delta H^\circ_v = 0.134T_b - 14.408 \ (n = 18, r = 0.999) \quad (6)$$

$$\Delta H^\circ_v = 0.175T_b - 29.681 \ (n = 16, r = 0.996) \quad (7)$$

hydrocarbon subclasses exhibit better correlation coefficients than eq 5 and that the slopes and intercepts of the individual plots differ markedly. It could be of interest to note that cyclohexylbenzene complies with the equation for alkylbenzenes (7) rather than eq (6) for alkylcycloalkanes. Namely, T_b(c-C_6H_{11}Ph) = 508.65 K, $(\Delta H^\circ_v)_{calc}$ from eq 7, 59.33 kJ/mol, $(\Delta H^\circ_v)_{calc}$ from eq 6, 53.75 kJ/mol; experimental ΔH°_v = 59.94 kJ/mol.

A general feature of these linear correlations is that they seem to accommodate data up to a certain limit. Data of alkyl derivatives with seven carbon atoms and higher usually exhibit a positive deviation from the regression line, i.e., 2 kJ/mol or higher. It is felt that this phenomenon is relevant to the observed concavity in the ΔH°_v vs T_b plot for the saturated hydrocarbons. An examination of the slopes of the regression equation, Table III, for the various classes of compounds indicates that there might be some connection between the magnitude of the slope and the characteristic group in the molecule. The largest slope is exhibited by the alcohols, and this can be readily attributed to the strong hydrogen bonding which occurs in this class of compounds. It appears reasonable to believe that the magnitude of the slope of the ΔH°_v vs T_b straight line reflects the energy that arises from nonbonded interactions between C–H bonds of the alkyl moiety and the characteristic group in the molecule. For example, a nonbonded interaction between C–H bonds of the alkyl group and the π-system of the phenyl ring in alkylbenzenes could explain the markedly higher slope in eq 7 as compared to that of cycloalkanes, eq 6, namely, 0.175 versus 0.134 kJ M^{-1} deg^{-1}.

The regression equations which are listed in Table III can be represented by an alternative form, eq 8, which is

$$(\Delta H_v - b)/T_b = a \quad (8)$$

reminiscent of Trouton's rule. Where, a = the slope of the ΔH°_v vs T_b straight line and b = the corresponding intercept. Both a's and b's are characteristic of a particular class of compounds, and the equation holds within certain limits.

Now if we bear in mind that enthalpies of vaporation of n-alkyl derivatives are linearly related to the corresponding enthalpies of formation, we are led to the conclusion that *the normal boiling points of organic compounds with normal alkyl chains are linearly related to*

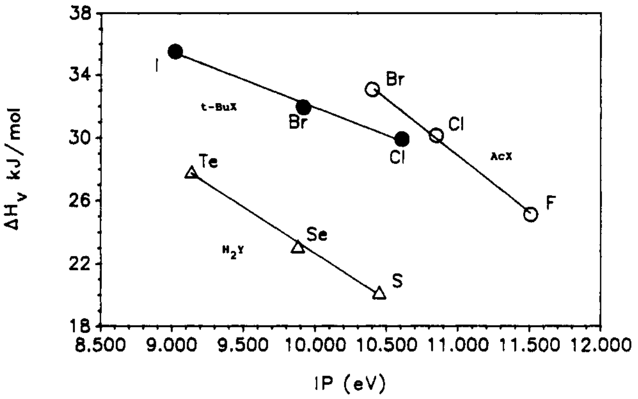

Figure 10. Standard enthalpies of vaporization at 298.15 K of *t*-BuX (from ref 14) and AcX (from ref 11) plotted against the respective ionization potentials (from ref 18a). Enthalpies of vaporization at the normal boiling point of chalcogen hydrides (from ref 16) plotted likewise.

the respective enthalpies of formation. In Figure 9 are plotted the standard enthalpies of formation[17] (*g*, 298.15 K) of C_2 up to C_6 alkanols and we notice that the above mentioned linearity holds indeed. An exciting feature of Figure 9 is that it contains more information than was expected. Namely, it appears as a cross-correlation with nearly parallel lines which imply the following: (a) The normal boiling points of the secondary alkyl derivatives within a homologous series are linearly related to the respective enthalpies of formation. The same is true for the normal boiling points of the *iso*- and *tert*-alkyl derivatives of the same homologous series. (b) The normal boiling points of alkyl derivatives having the same carbon number but different alkyl branching are linearly related to the corresponding enthalpies of formation. It is felt that analogous relationships hold for the normal boiling points and the enthalpies of formation of every class of compounds, and plots like Figure 9 may function as a check for the internal consistency of the data involved. (c) The group $(CH_3)_2CH$ according to the correlation in Figure 9 is a secondary rather than an *iso*-alkyl. This agrees with the results given in Table II.

Enthalpies of Vaporization and Ionization Potentials. Enthalpies of vaporization of sequences of compounds RX (X = halogen) seem to plot linearly against the respective ionization potentials, IP(RX),[17] e.g. Figure 10, for *t*-BuX (X = Cl, Br, and I) and for AcX (X = F, Cl, and Br). The data for the sequence of PhX (X = F, Cl, Br, and I) do not plot linearly. We notice that the range of the structural effect in IP's for the sequence of *t*-BuX (from X = Cl to X = I) is 1.59 eV, whereas, in the sequence of PhX (from X = Cl to X = I) is only 0.37_5 eV. Obviously, the lower value of the structural effect in the series of PhX is due to the fact that ionization of PhX involves a $PhX^{\bullet+}$ species which is isoconjugate to $PhCH_2^+$ or to $PhCH_2^{\bullet}$ and, therefore, it is delocalized. This is in contrast to the behavior of alkyl halides, whose ionization involves localized $RX^{\bullet+}$ species. It is felt that this is the reason for the different behavior of the two sets of data. The scarcity of the data does not permit the substantiation of the $\Delta H°_v$ vs IP correlation. However, it seems probable that enthalpies of vaporization of derivatives of elements that belong to the same group plot linearly against the respective IP's. The hydrides of chalcogens, with the exception of H_2O, which exhibits strong hydrogen bonding, plot linear with respect to the corresponding ionization potentials, Figure 10. An estimate of the ionization potential of AcI can be obtained from the appropriate correlation in Figure 10, by extrpolation to its enthalpy of vaporization, 38.493 kJ/mol. The estimated value is IP(AcI) = 9.7 eV.

Transferability of Alkyl Group and/or Molecular Fragment Contribution to the Enthalpy of Vaporization. The linearity between the enthalpy of vaporization of any two series of organic compounds implies that the alkyl group contribution to the enthalpy of vaporization may be transferable and/or additive. For example, if we consider the redistribution reaction (9) and assume that

$$\underset{1}{s\text{-BuBr}} + \underset{2}{n\text{-}C_5H_{11}I} \rightarrow \underset{3}{s\text{-BuI}} + \underset{4}{n\text{-}C_5H_{11}Br} \qquad (9)$$

transferability is operable, then we can obtain an estimate of the enthalpy of vaporization of, e.g., *s*-BuI from the corresponding values of *n*-BuBr, *n*-C_5H_{11}I, and *n*-C_5H_{11}Br. Namely:

$$\Delta H°_v(3) = \Delta H°_v(1) + \Delta H°_v(2) - \Delta H°_v(4) = 34.51 + 45.27 - 41.31 = 38.47 \text{ kJ/mol}$$

(experimental: 38.49)

As an example of transferability of a molecular fragment contribution to the enthalpy of vaporization, we consider the disproportionation, eq 10.

$$\underset{5}{2Cl(CH_2)_3Cl} \rightarrow \underset{6}{Cl(CH_2)_4Cl} + \underset{7}{ClCh_2CH_2Cl} \qquad (10)$$

$$\Delta H°_v(5) = 0.5|\Delta H°_v(6) + \Delta H°_v(7)| = 0.5(46.36 + 35.22) = 40.79 \text{ kJ/mol}$$

(experimental: 40.79)

Transferability of alkyl group or molecular fragment contribution to the enthalpy of vaporization is not limited to the organic halogen compounds only. In fact it is shown to hold for ethers, sulfides, ketones, and esters as well. Relevant examples are given below, eqs 11–14. Table IV

$$\underset{8}{2EtOPr\text{-}n} \rightarrow \underset{9}{Et_2O} + \underset{10}{n\text{-}Pr_2O} \qquad (11)$$

$$\Delta H°_v(8) = 0.5|\Delta H°_v(9) + \Delta H°_v(10)| = 0.5(27.37 + 35.79) = 31.58 \text{ kJ/mol}$$

(experimental: 31.57)

$$\underset{11}{2s\text{-PrSPr-}n} \rightarrow \underset{12}{s\text{-}Pr_2S} + \underset{13}{n\text{-}Pr_2S} \qquad (12)$$

$$\Delta H°_v(11) = 0.5|\Delta H°_v(12) + \Delta H°_v(13)| = 0.5(39.64 + 44.23) = 41.94 \text{ kJ/mol}$$

(experimental: 41.81)

$$\underset{14}{2MeCOPr\text{-}s} \rightarrow \underset{15}{Me_2CO} + \underset{16}{s\text{-}Pr_2CO} \qquad (13)$$

$$\Delta H°_v(14) = 0.5|\Delta H°_v(15) + \Delta H°_v(16)| = 0.5(31.27 + 41.57) = 36.42 \text{ kJ/mol}$$

(experimental 36.87)

$$\underset{17}{CH_3COOMe} + \underset{18}{CH_3CH_2COOEt} \rightarrow \underset{19}{CH_3COOEt} + \underset{20}{CH_3CH_2COOMe} \qquad (14)$$

$$\Delta H°_v(19) = \Delta H°_v(17) + \Delta H°_v(18) - \Delta H°_v(20) = 32.50 + 39.27 - 35.69 = 36.08 \text{ kJ/mol}$$

(experimental: 35.95)

summarizes the examples given above along with additional ones.

Trouton's Ratios. The ratio of the enthalpy of vaporization, either the standard one at 298.15 K or at the boiling point, and the normal boiling point in Kelvin degrees of organic compounds exhibits a marked dependence

Table IV. Transferability–Additivity of Alkyl Group Contribution to the Enthalpy of Vaporization of Alkyl Halides, Ethers, Sulfides, Amines, Ketones, and Esters

redistribution reaction	standard enthalpy of vaporization, kJ M^{-1}		
	estimated (at 298.15 K)		experimental
s-PrI[a] + *n*-C_5H_{11}Br → *s*-PrBr + *n*-C_5H_{11}I	38.47	(−0.02)[b]	38.49
s-BuCl + *t*-BuI → *s*-PrI + *t*-BuCl	32.18	(+0.50)	31.68
s-BuCl + *i*-BuI → *s*-PrI + *i*-BuCl	31.44	(−0.24)	31.68
s-BuCl + *n*-BuI → *s*-PrI + *n*-BuCl	31.45	(−0.23)	31.68
$2Cl(CH_2)_3Cl \rightarrow Cl(CH_2)_4Cl + Cl(CH_2)_2Cl$	40.79	(0.00)	40.79
$2Br(CH_2)_3Br \rightarrow Br(CH_2)_4Br + Br(CH_2)_2Br$	47.42	(−0.04)	47.46
2EtOPr-*n* → Et_2O + *n*-Pr_2O	31.58	(+0.01)	31.57
2*n*-PrOBu-*n* → *n*-Pr_2O + *n*-Bu_2O	40.40	(+0.14)	40.26
s-PrOPr-*n* → *s*-Pr_2O + *n*-Pr_2O	34.03	(+0.08)	33.95
n-$PrOCH_2CH_2OMe$ → *n*-$PrO(CH_2)_2OPr$-*n* + $MeOCH_2CH_2OMe$	43.55	(−0.12)	43.67
2*s*-PrSPr-*n* → *s*-Pr_2S + *n*-Pr_2S	41.95	(+0.14)	41.81
2EtSBu-*n* → Et_2S + *n*-Bu_2S	44.42	(−0.11)	44.53
2MeSBu-*n* → Me_2S + *n*-Bu_2S	40.43	(−0.07)	40.50
2*n*-PrSH → *n*-Pr_2S + H_2S	32.19	(+0.14)	32.05
2EtSH → Et_2S + H_2S	28.01	(+0.49)	27.52
2(Et)(*s*-Pr)NH → Et_2NH + *s*-Pr_2NH	33.10	(−0.15)	33.25
2(*n*-Pr)(*s*-Pr)NH → *n*-Pr_2NH + *s*-Pr_2NH	37.41	(+0.11)	37.30
2(Me)(*s*-Pr)NH → Me_2NH + *s*-Pr_2NH	30.08	(−0.85)	30.93
2MeCOPr-*s* → Me_2CO + *s*-Pr_2CO	36.42	(−0.45)	36.87
2MeCOEt → Me_2CO + Et_2CO	34.98	(+0.06)	34.92
2c-PrCOMe → c-Pr_2CO + Me_2CO	42.49	(+3.02)	39.47
2MeCOBu-*n* → Me_2CO + *n*-Bu_2CO	42.29	(−0.86)	43.15
2EtCOPr-*s* → Et_2CO + *s*-Pr_2CO	40.13	(+0.27)	39.86
MeCOOMe + EtCOOEt → MeCOOEt + EtCOOMe	32.37	(−0.13)	32.50
MeCOOMe + *n*-BuCOOEt → MeCOOEt + *n*-BuCOOME	31.81	(−0.69)	32.50
HCOOMe + MeCOOMe → HCOOEt + MeCOOMe	28.92	(+0.32)	28.60
HCOOBu-*n* + MeCOOEt → HCOOEt + MeCOOBu-*n*	40.31	(−0.85)	41.16

[a] The indicated estimated and experimental values are referred to the first compound in the redistribution reaction. [b] Difference between estimated and experimental enthalpy of vaporization.

Table V. Regression Equations of $\Delta H^\circ_v/T_b$ (kJ M^{-1} deg^{-1}) vs *n* (or Σn) Correlations[a]

sequence	regression equation	*r*	range of *n*
n-RCl	$10^3(\Delta H^\circ_v/T_b) = 4.894n + 75.647$	0.9995	3–8, 12, 16
n-RBr	$10^3(\Delta H^\circ_v/T_b) = 4.701n + 79.562$	0.9994	1–8, 12, 16
n-RI	$10^3(\Delta H^\circ_v/T_b) = 4.222n + 84.101$	0.9996	2–6
n-ROH	$10^3(\Delta H^\circ_v/T_b) = 5.279n + 110.690$	0.9953	1–10
n-RSH	$10^3(\Delta H^\circ_v/T_b) = 4.772n + 79.641$	0.9999	2–5, 10
n-R^1OR^2-*n*	$10^3(\Delta H^\circ_v/T_b) = 4.938\Sigma n + 69.211$	0.9898	2, 4, 4, 5, 5, 6, 6, 6, 7, 7, 7, 8, 8
n-R^1SR^2-*n*	$10^3(\Delta H^\circ_v/T_b) = 4.315\Sigma n + 81.063$	0.9971	2, 3, 4, 4, 5, 5, 6, 6, 6, 8
n-$ROCH_2CH_2OH$	$10^3(\Delta H^\circ_v/T_b) = 4.750n + 108.910$		1–3
n-RNH_2	$10^3(\Delta H^\circ_v/T_b) = 4.426n + 84.759$	0.9993	1–7
n-R_2NH	$10^3(\Delta H^\circ_v/T_b) = 3.980\Sigma n + 81.577$	0.9910	2, 4, 6, 6, 8
n-R_3N	$10^3(\Delta H^\circ_v/T_b) = 3.881\Sigma n + 72.800$		3, 6, 9
n-R^1COR^2-*n*	$10^3(\Delta H^\circ_v/T_b) = 4.815\Sigma n + 83.767$	0.9968	2, 3, 4, 4, 5, 5, 6, 8, 10, 11
n-ROAc	$10^3(\Delta H^\circ_v/T_b) = 3.872n + 94.425$	0.9992	1–4
n-RCN	$10^3(\Delta H^\circ_v/T_b) = 4.593n + 87.840$	0.9978	1–11
n-RH	$10^3(\Delta H^\circ_v/T_b) = 5.294n + 61.390$	0.9993	5–16

[a] Standard enthalpies of vaporization at 298.15 K were used in the correlations.

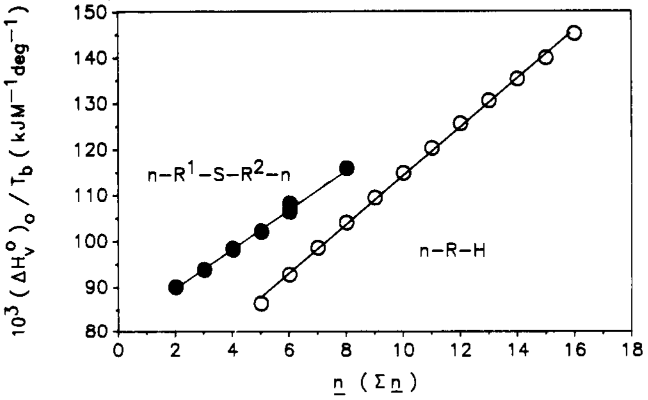

Figure 11. Trouton's ratios (standard enthalpy of vaporization at 298.15 K over the normal boiling point in Kelvin) of normal hydrocarbons and of di-*n*-alkyl sulfides plotted against the respective carbon numbers or sum of carbon numbers.

upon its structure. In many respects Trouton's ratios behave like ordinary thermochemical data. For example, Trouton's ratio of homologous series of compounds with normal alkyls exhibit the usual linearity with respect to the corresponding carbon number or sum of carbon numbers, e.g. Figure 11. It should be pointed out that the ratio of the enthalpy of vaporization, either the standard one at 298.15 K or at the boiling point, and the normal boiling point plots linear against the respective carbon number or sum of carbon numbers. Table V summarizes the regression equations of the $(\Delta H^\circ_v)_0/T_b$ vs *n* or Σn correlations for various classes of organic compounds. In these correlations the standard enthalpies of vaporization at 298.15 K were used. By analogy to the ΔH_v vs *n* or Σn correlations we note that the slope of the regression line represents the contribution of the methylene group to the Trouton's ratio of a compound $H(CH_2)_nY$ and the intercept the Trouton's ratio of the "parent" compound HY. For example, from the series of the *n*-alkyl chlorides the Trouton's ratio of HCl is estimated as 0.07565 kJ M^{-1} deg^{-1} and this should be compared with the ratio 17.53/188.25 = 0.0931. The two numbers agree to within 19%. One can

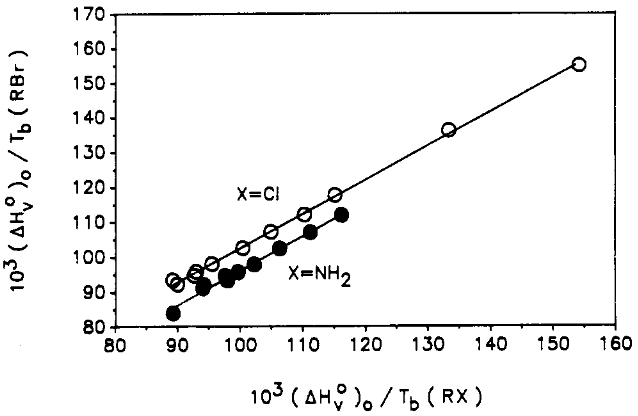

Figure 12. Trouton's ratios of alkyl bromides plotted against the respective Trouton's ratios of alkyl chlorides and of alkylamines.

attribute this rather poor agreement to the fact that the estimated and the experimental values are not at the same conditions. Namely, the estimated value is derived from standard enthalpies of vaporization at 298.15 K, whereas for the calculation of the experimental ratio the enthalpy of vaporization at the normal boiling point was used. An additional reason for the poor agreement between estimated and experimental Trouton's ratios could be the involvement of a considerable error both in the enthalpies of vaporization and the normal boiling points. An indication of the soundness of this analysis may be illustrated by the following: If we devide the intercept of the ΔH_v vs n regression line by the intercept of the $\Delta H_v/T_b$ vs n plot, we should obtain the normal boiling point of the parent compound HY. Indeed, in the case of normal hydrocarbons the ratio is equal to 18.5; the normal boiling point of H_2 = 14.01 K. The agreement is quite satisfactory. Similarly, from the series of n-alkyl chlorides we estimate the normal boiling point of HCl to −87.5 °C, which agrees within 2.6 degrees with the experimental one, −84.9 °C. Less satisfactory agreement between the estimated boiling point and the experimental one of the "parent" compound have been obtained from the series of n-R_2CO, for H_2CO, estimated, −26.6 °C, experimental, −21.0 °C; from the series of n-RCN, for HCN, estimated 32.8 °C, experimental 26.0 °C; from the sequence of n-RSH, for H_2S, estimated −50.0 °C, experimental −60.7 °C.

The linearity between Trouton's ratios and the respective carbon numbers implies that Trouton's ratios of any two series n-RX and n-RY of compounds should be linearly related to each other. Indeed, this seems to be the case, for example, between RCl and RBr and even RBr and RNH_2, Figure 12. Interestingly enough, the plots include also the branched alkyl compounds. However, Trouton's ratios of alcohols do not plot linearly against, e.g., the respective data of alkyl bromides, Figure 13. This is an interesting contrast between alcohols and amines both of which exhibit hydrogen bonding. The lack of linearity in the case of alcohols could be atrributed to the occurrence of much stronger hydrogen bonding as compared to primary amines.

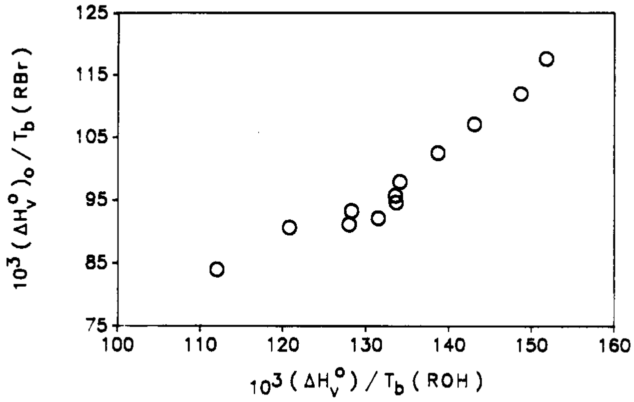

Figure 13. Trouton's ratios of alkyl bromides plotted against the Trouton's ratios of the respective alkanols.

Method for Estimating Normal Boiling Points of Organic Compounds with Straight Alkyl Chains. Normal boiling points of organic compounds of relatively high molecular weight are almost nonexistent. Indeed, the various compilations of boiling points of organic compounds usually quote the boiling point of a high-boiling compound at a reduced pressure. For theoretical reasons, however, knowledge of the normal boiling point could be required. Therefore, we propose the following rather general method for obtaining an estimate of the boiling point from a limited amount of thermochemical data. The method is based on the above mentioned linearity between enthalpy of vaporization and the respective carbon number, on the one hand, and the linearity between Trouton's ratio and the corresponding carbon number, on the other. Namely, in order to obtain an estimate of the boiling point of a given compound, we need (a) its enthalpy of vaporization and (b) the respective Trouton's ratio. The ratio of these two parameters should be equal to the normal boiling point of the compound. For example, for estimating the boiling point of n-$C_{14}H_{29}Cl$, we calculate from the appropriate regression equation of Table I a value of ΔH°_v by introducing n = 14. This gives the estimate: 81.57 kJ/mol. Likewise, from the corresponding regression equation from Table V, we obtain the estimate $\Delta H^\circ_v/T_b$ = 0.1442 kJ M^{-1} deg^{-1}. Therefore, T_b(n-$C_{14}H_{19}Cl$) = 566 K or (293 °C). Experimental bp 292 °C. Some additional examples: n-$C_{18}H_{37}Cl$, estimated 343 °C, experimental 348 °C; n-$C_{20}H_{41}Cl$, estimated 364 °C, experimental 373 °C; n-$C_{18}H_{37}Br$, estimated 356 °C, experimental 362 °C; n-$C_{20}H_{41}Br$, estimated 378 °C, experimental 386 °C. It can be seen that the agreement between estimated and experimental boiling points is within 8 degrees or better.

Supplementary Material Available: Thermochemical data used in correlations shown in Figures 1–13 (5 pages). Ordering information is given on any current masthead page.