Estimations of the heats of vaporization of simple hydrocarbon derivatives at 298 K

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(5c), and 1,3-dimethyl-5-formyluracil (5d) [mp 125–126 °C (lit.[14] mp 126–127 °C)]. A small amount of 5,5'-[oxybis(methylene)]-bis(1,3-dimethyluracil) (7d) was further obtained from the reaction of 1d. The spectral and analytical data of 5c and 7d are given below.

5c: mp 202–205 °C; NMR (DMSO-d_6) δ 3.20 (s, 3 H), 8.17 (s, 1 H), 9.87 (s, 1 H), 12.16 (broad, 1 H); IR (Nujol) 3130, 1730 (sh), 1685, 1610, 1590 cm^{-1}; mass spectrum, m/e (relative intensity) 154 (12), 126 (100), 69 (62). Anal. Calcd for $C_6H_6N_2O_3$: C, 46.76; H, 3.92; N, 18.18. Found: C, 46.61; H, 3.95; N, 17.95.

7d: mp 182–184 °C; NMR (CDCl$_3$) δ 3.34 (s, 6 H), 3.42 (s, 6 H), 4.35 (d, 4 H, $J = 1$ Hz), 7.39 (t, 2 H, $J = 1$ Hz); IR (Nujol) 1700, 1660, 1640 cm^{-1}; mass spectrum, m/e (relative intensity) 323 (0.1), 170 (9), 169 (100), 154 (22), 153 (46). Anal. Calcd for $C_{14}H_{18}N_4O_5$: C, 52.17; H, 5.63; N, 17.38. Found: C, 52.64; H, 5.67; N, 17.14.

Treatment of 4d (1 mmol) with Na$_2$S$_2$O$_8$ (1 mmol) was also carried out according to the procedure described above to give 4d (0.20 mmol) and 5d (0.72 mmol). Reaction of 5d (1 mmol) with Na$_2$S$_2$O$_8$ (1 mmol) gave 5d (0.53 mmol) and 1,3-dimethyl-uracil-5-carboxylic acid (6d)[34] (0.11 mmol).

Oxidation of Thymines 1a,d by Potassium Peroxomonosulfate. Oxone, which is a mixture of KHSO$_5$, KHSO$_4$, and K$_2$SO$_4$ (2:1:1), obtained from DuPont was used as potassium peroxomonosulfate. A solution (pH 2.4) of 1a (1 mmol) and KHSO$_5$ (2 mmol) in water (50 mL) was heated or stirred at room temperature. The reaction mixture (pH 2.0) was evaporated to give a residue that was extracted with acetone. The extract was evaporated and chromatographed (silica gel TLC, developed with ethyl acetate) to give 5-hydroxy-5-methylbarbituric acid (9a) [dec 225–227 °C (lit.[24] 226–227 °C)] and cis-5,6-dihydroxy-5,6-dihydrothymine (8a) [dec 212–216 °C (lit.[24] 215–216 °C)]: NMR (DMSO-d_6) δ 1.28 (s, 3 H), 4.35 (t, 1 H, $J = 5$ Hz), 5.23 (s, 1 H), 5.98 (d, 1 H, $J = 5$ Hz), 8.1 (broad, d, 1 H, $J = 5$ Hz), 10.05 (broad, 1 H).

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Oxidation of 1d (1 mmol) by KHSO$_5$ (1 or 2 mmol) in water (50 mL) was also carried out according to the procedure described above to give 1,3-dimethylparabanic acid (10d) [mp 151–153 °C (lit.[35] mp 151–153 °C)], 1,3-dimethyl-5-hydroxy-5-methylbarbituric acid (9d) [mp 106–107 °C (lit.[36] mp 107 °C)], 5d, and cis-5,6-dihydroxy-1,3-dimethyl-5,6-dihydrothymine (8d)[6] (oil): NMR (DMSO-d_6) δ 1.25 (s, 3 H), 2.95 (s, 3 H), 3.00 (s, 3 H), 4.50 (s, 1 H), 5.6 (broad, 1 H), 6.5 (broad, 1 H).

***cis*-6-Hydroperoxy-5-hydroxy-5,6-dihydrothymine (11a).** A solution of 1a (1 mmol), KHSO$_5$ (2 mmol), and H$_2$O$_2$ (4 mmol) in water (50 mL) was stirred at room temperature for 24 h. The reaction mixture was evaporated and chromatographed (silica gel TLC, developed with ethyl acetate) to give 11a (0.34 mmol): NMR (DMSO-d_6) δ 1.34 (s, 3 H), 4.60 (d, 1 H, $J = 5$ Hz), 5.28 (s, 1 H), 8.27 (broad, d, 1 H, $J = 5$ Hz), 9.99 (broad, 1 H), 11.58 (s, 1 H); (acetone-d_6) δ 1.50 (s, 3 H), 4.28 (s, 1 H), 4.88 (d, 1 H, $J = 5$ Hz), 7.6 (broad, 1 H, $J = 5$ Hz), 9.1 (broad, 1 H), 10.98 (s, 1 H). Treatment of 11a with DMSO-d_6 in a NMR tube led to the formation of 8a. Compound 11a was also prepared in 40% yield by treatment of 8a (1 mmol) with H$_2$O$_2$ (4 mmol) in 0.1 M HCl (50 mL) at room temperature for 24 h according to the method reported by Hahn and Wang.[21]

5-Hydroxy-6-methoxy-5,6-dihydrothymine (12a). A solution of 1a (1 mmol) and KHSO$_5$ (2 mmol) in water (50 mL) was heated at 80 °C for 7 h. The reaction mixture was evaporated to give a residue that was treated with methanol (20 mL) at room temperature for 24 h. The solution was evaporated and chromatographed (silica gel TLC, developed with ethyl acetate) to give 12a (0.47 mmol): mp 190–194 °C (lit.[28] mp 195 °C).

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Estimations of the Heats of Vaporization of Simple Hydrocarbon Derivatives at 298 K

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A simple method of estimating the enthalpies of vaporization of monofunctional hydrocarbon derivatives within 5% of literature values is described. The technique utilizes the analytical expression previously developed to estimate vaporization enthalpies of hydrocarbons, $\Delta H_v = 1.12\bar{n}_c + 0.31n_Q + 0.71$, where n_Q and $\bar{n}_c$ refer to the number of quaternary and nonquaternary carbon atoms, respectively, modified by introducing an additional parameter, b, that is characteristic of the functional group in question. Values of b for 21 different functional groups are derived from 433 critically reviewed vaporization enthalpies. They range from a low value of 1.19 kcal/mol for ethers to a high value of 12.74 kcal/mol for sulfones. Results obtained by other estimation techniques are compared. Advantages of this method include the ease with which estimations can be made, the general applicability of the method to compounds of diverse structure, and the overall accuracy of the estimations. In addition, the magnitude of b, a characteristic of the attractive interactions of a functional group, can be correlated to E_T values that are often used as a measure of solvent polarity.

Many studies of organic systems reference the gas phase as a standard state. Evaporation enthalpies[1] are an important physical property of the condensed phase, and some reliable measure of this quantity is a necessary requirement for such studies.[2] The large number of new

(1) The term "evaporation enthalpies" is used here to denote both enthalpies of vaporization (liquids) and enthalpies of sublimation (solids).

(2) See, for example: Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

compounds that are reported annually far exceeds the few compounds whose evaporation enthalpies are reported. This makes it improbable that an evaporation enthalpy for a desired compound can be found in the literature. Additional complications can arise when evaporation enthalpies are reported in conjunction with other work. Sufficient experimental data may not be reported in these studies, making it difficult to assess reliability of the measurements. In turn, these enthalpies may also be missed by the abstracting services. It is also possible to find many examples of experimental results on the same material with large discrepancies in reported values. This is particularly the case if the materials in question are of low volatility.[3,4] Some rational means of identifying the most reliable value from a series of discordant values would be of considerable value in this respect such as was done in ref 4 for diphenylmethane.

One approach to solving the problems outlined above relies on the development of reliable estimation techniques that can be used in conjunction with experimental data, if the data are available, or in place of experimental data if there are none, to establish reasonable limits for these enthalpies. Several techniques have been developed for estimating evaporation enthalpies. Some of these techniques require knowledge of the physical properties of the material in question.[5] These techniques may not be of much value if the material in question is unavailable or the necessary physical constants are difficult to measure. Additionally, application of some of these techniques may also be complex and tedious.[6]

Other techniques require only structural information.[7,8] The focus of some of such work has been on accuracy, rather than on general applicability. This has led to the development of estimation techniques with rather restrictive structural requirements that severely limit their general applicability. Semiempirical theoretical calculations using atomic pair potentials have also been used to calculate vaporization energies.[9] Recently, Guthrie and Taylor[10] reported an estimation technique based on bond additivity and, along with DuCros et al.,[11] reported similar estimation methods based on group additivity parameters. From Guthrie and Taylor's work, data from 388 compounds could be fitted with 57 parameters. The development of group additivity parameters promises to be a reliable method of estimating vaporization enthalpies. This method is limited at present, despite the large number of vaporization enthalpies available, because of the lack of sufficient reliable data representative of the breadth of structural fragments frequently encountered in organic chemistry.

We have previously reported a simple relationship that could be used to estimate the enthalpies of vaporization of 138 hydrocarbons of diverse structure.[12] This relationship, eq 1, consists of three parameters and is able to reproduce the heats of vaporization of liquid hydrocarbons within 5% of accepted literature values. Subsequently, we have also reported on a method referred to as SEALE (semiempirical additivity of latent enthalpies) that uses this relationship along with experimental heats of fusion to estimate heats of sublimation of solid hydrocarbons.[4] The accuracy of SEALE is also of the order of 5%. We now report that eq 1 can also be modified to successfully estimate the enthalpies of vaporization of a variety of simple liquid hydrocarbon derivatives. Our purpose for doing so in the light of previous work is to demonstrate that the relationships derived from eq 1 can be used in circumstances where a group parameter may not be available. In addition, the relationships derived from eq 1 are more general and easier to use. Furthermore, these estimations can be accomplished without a sacrifice in accuracy. As an added bonus, this approach generates a series of constants characteristic of the functional group present. These constants may provide a useful alternative "group measure" of solvent polarities.

The enthalpy of vaporization equation that we previously reported for liquid hydrocarbons at 298 K is given by eq 1[12]

$$\Delta H_v = 1.12\bar{n}_c + 0.31n_Q + 0.71 \tag{1}$$

$$\Delta H_v = 1.12\bar{n}_c + 0.31n_Q + b + 0.71 \tag{2}$$

where n_Q is the number of quaternary carbon atoms, $\bar{n}_c$

Table I

compd class	intercept b	no. of entries	range of entries	av dev %	x
hydrocarbons		138	C_4–C_{13}		
alcohols	7.02	31	C_1–C_{14}	3.1	1.01
aldehydes	3.08	7	C_2–C_7	4.3	0.98
amides (N-substituted)	10.16	8	C_2–C_6	1.9	0.90
amines (primary)	3.54	16	C_1–C_7	6.5	0.99
amines (secondary)	2.12	13	C_4–C_{10}	4.9	1.00
bromides	3.43	16	C_1–C_{16}	2.8	0.96
carboxylic acids	9.27	10	C_1–C_9	2.7	1.01
chlorides	2.59	22	C_3–C_{18}	3.1	1.02
disulfides	5.32	5	C_4–C_8	2.6	0.91
esters	2.50	64	C_4–C_{16}	4.6	0.97
ethers	1.19	56	C_4–C_{12}	5.7	0.91
iodides	4.30	17	C_2–C_{10}	3.6	0.95
ketones	2.50	38	C_5–C_{12}	5.6	0.92
nitriles	3.98	31	C_3–C_{14}	3.3	0.95
nitro compounds	5.44	9	C_3–C_8	4.6	0.80
pyridines	2.91	12	C_5–C_8	4.2	0.65
sulfides	3.20	41	C_3–C_{12}	4.5	0.84
sulfoxides	10.13	4	C_2–C_6	3.0	1.30
sulfones	12.67	6	C_4–C_8	5.0	1.04
thioesters	4.03	5	C_4–C_6	2.4	0.76
thiols	3.32	22	C_2–C_{10}	3.4	1.03

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is the number of nonquaternary carbon atoms, and 0.71 is numerically close to the value of RT at 298 K.[13] Equation 1 can be modified to include the various hydrocarbon derivatives listed in column 1 of Table I by simply adding in the constant term, b, of column 2, Table I. Equation 2 with the aid of the constants in Table I is also able to reproduce the vaporization enthalpies of monosubstituted hydrocarbon derivatives typically within 5%. Column 1 in Table I includes all the functional groups for which we have been able to find reliable experimental data.[14] The second column in this table summarizes the magnitude of the constant term that is necessary to correct for the functional group in question. The number of data points used to generate the constant is listed in the third column, and an indication of the breadth of molecular size covered in the correlation is included in the fourth column. It should be noted that the intercept was generated from all available data and as such is applicable to molecules of diverse structures, provided that only a single functional group is present. The fifth column reports the average absolute deviation of ΔH_v between calculated and experimental data. This number was generated by averaging the absolute value of each deviation. As noted in this column, eq 2 is able to reproduce ΔH_v to about 5%. As discussed below, a comparison of the trends observed between calculated and experimental results suggests that further fine tuning of this equation is likely to improve both the accuracy and applicability. The final column, x, is a measure of the linearity observed in the correlation and is discussed below.

The basis of our analysis is derived from the assumption that vaporization enthalpies are group properties and as such can be derived from a simple additivity of the contributions of each group. We have previously demonstrated that vaporization enthalpies for hydrocarbons can be estimated quite accurately by using the three parameters of eq 1 and are not subject to significant perturbations caused by changes in molecular structure, except as noted. Therefore, the constant term, b, for each functional group listed in Table I was derived from eq 3 by sub-

$$b = \Delta H_v(\text{exptl}) - \Delta H_v(\text{hydrocarbon}) \qquad (3)$$

tracting out the contribution of the enthalpy of the hydrocarbon portion of the molecule from the experimental vaporization enthalpy for each compound. The remainder was then averaged and used to generate a value for b. The vaporization enthalpy for the hydrocarbon portion of the molecule was estimated by using eq 1. It was noted that curvature was sometimes observed in a plot of $\Delta H_v(\text{exptl})$ versus $\Delta H_v(\text{calcd})$ at the low end of the ΔH_v values. This gave rise to a $\Delta H_v(\text{exptl})/\Delta H_v(\text{calcd})$ value of >1 as the series converged to the value of the functional group, b. This effect, although attenuated, was also observed with hydrocarbons.[12] To correct for this curvature and to
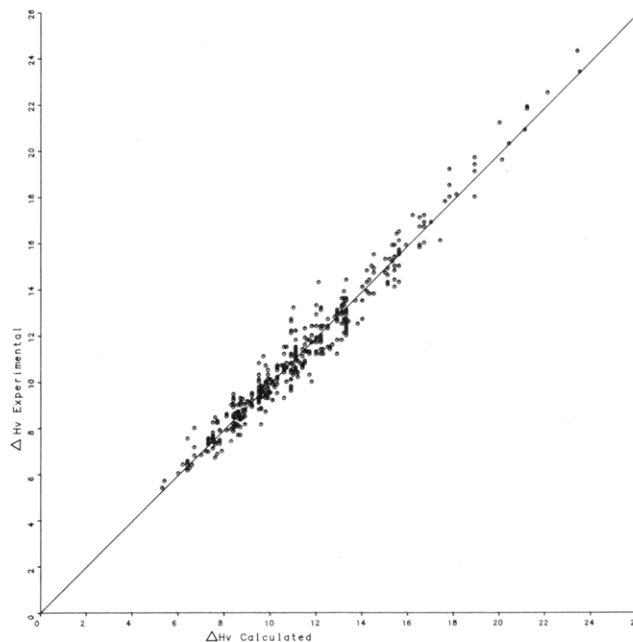

Figure 1. Heats of vaporization: experimental vs calculated.

prevent small molecules from having a disproportionately large effect on the value of b, the following protocol was followed. First, a value of b was generated from all available data and the calculated and experimental ΔH_v values were compared. If the average deviation of the smallest members of the series as a group (by carbon count) exceeded 5% (the scatter typically observed in this study), then these values were discarded and a new value of b was recalculated. Generally, one or two ΔH_v values usually belonging to C_1 and/or C_2 molecules were ignored by this treatment (molecules whose vaporization energies were not included in evaluation of b are so indicated in the supplementary tables). The new value of b generated in this manner was usually only slightly smaller than the original and is the value reported in Table I. For two compounds, the calculated and experimental values differed by more than 20% of the experimental value. For the reason noted above, these values were also not used in the correlation although they are included in the supplementary tables. Of the 433 compounds correlated in this study, 35 compounds exhibited deviations between 10 and 20% of the experimental value; the remainder showed deviations of $<10\%$. Some idea of the nature of the correlation observed can be obtained from examination of Figure 1. This figure contains data for all the molecules included in the correlation. The equation for the straight line by least-squares fit is given by

$$\Delta H_v(\text{exptl}) = 0.9959 \Delta H_v(\text{calcd}) + 0.037 \qquad (4)$$

with a correlation coefficient of 0.9809.

The range of carbon atoms and the number of experimental data points available for the generation of b differ for each functional group in Table I. This obviously affects the reliability of eq 2 in estimating vaporization enthalpies for molecules containing any particular functional group. For example, the lack of sufficient data for molecules such as disulfides and sulfoxides renders the value of the intercept for these molecules more uncertain. The use of eq 2 for these molecules must take this into account.

As a test of the linearity of the observed fit, we have computed the best power, x, of a least-squares fit of ln $[\Delta H_v(\text{exptl}) - b - 0.71]$ vs ln $[\tilde{n}_c + 0.31 n_Q]$. The calculated value of x can be used as a measure of the linearity of the

(13) The constant term in eq 1, 0.71, has been interpreted as being approximately RT at 298 K.[12] This does not imply that this equation could be used to correct calculated ΔH_v values to other temperatures. This relationship was derived from experimental data corrected to 298 K and is only valid at this temperature. For reasons of accuracy and to avoid possible confusion, we have employed the value of 0.71 in these relationships. The coefficients of $\tilde{n}_c$ and n_Q are expected to be temperature dependent.

(14) All the experimental data used in this work have been critically reviewed.[15,16] All data used are from ref 15, unless otherwise noted.

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Table II. Heats of Vaporization (298 K)

compd		ΔH_v			
		exptl	calcd by eq 2	from ref 6	from ref 10
C_4H_9Cl	1-chlorobutane	8.0	7.8	8.0	8.0
C_4H_9Cl	(+)-2-chlorobutane	7.53	7.8	7.6	NA
C_4H_9Cl	1-chloro-2-methylpropane	7.58	7.8	NA[a]	7.6
C_4H_9Cl	2-chloro-2-methylpropane	6.93	7.0	7.0	NA
$C_5H_{11}Cl$	1-chloropentane	9.13	8.9	9.1	9.2
$C_5H_{11}Cl$	2-chloropentane[b]	8.6	8.9	8.7	NA
$C_5H_{11}Cl$	1-chloro-3-methylbutane	8.8	8.9	NA	8.9
$C_5H_{11}Cl$	2-chloro-2-methylbutane	8.0	8.1	8.3	NA
C_6H_5Cl	chlorobenzene	9.63	10.0	10.2	9.6
$C_6H_{11}Cl$	chlorocyclohexane	10.4	10.0	NA	NA
$C_6H_{13}Cl$	1-chlorohexane[b]	10.2	10.0	10.3	10.4
C_5H_9N	pentanenitrile	10.6	10.3	10.6	10.9
C_6H_7N	1-cyanobicyclo[2.1.0]pentane	10.6	10.6	NA	NA
C_6H_7N	1-cyanocyclopentene	10.8	11.4	NA	11.2
$C_6H_{11}N$	hexanenitrile[b]	11.5	11.4	11.5	12.1
C_7H_5N	benzenecarbonitrile	12.5	12.5	NA	NA
C_7H_9N	1-cyanobicyclo[3.1.0]hexane	10.4	11.7	NA	NA
C_7H_9N	1-cyanocyclohexene	12.8	12.5	NA	12.4
$C_7H_{11}N$	cyanocyclohexane	12.4	12.5	NA	12.1
$C_7H_{13}N$	heptanenitrile	12.4	12.5	12.4	13.3
$C_8H_{15}N$	octanenitrile[b]	13.6	13.7	13.3	14.5
$C_{10}H_{19}N$	decanenitrile[b]	16.0	15.9	14.9	16.9
$C_{11}H_{21}N$	undecanenitrile[b]	17.0	17.0	15.7	18.1
$C_{12}H_{23}N$	dodecanenitrile[b]	18.2	18.1	16.6	19.4
$C_{14}H_{27}N$	tetradecanenitrile[b]	20.4	20.4	18.1	21.8

[a] NA = not available. [b] Reference 16.

observed correlation. Results of x for each functional group are listed in the last column of Table I. Linearity is suggested for most of the functional groups. Notable exceptions include the nitro compounds, sulfoxides, thiol esters, and pyridines. In all cases, the lack of correlation can presently be attributed to the paucity of reliable experimental data and to the small range of molecular size included in the correlation.

As an aid to the use of eq 2 in estimating vaporization enthalpies and to illustrate the typical correlation observed within a given functional group, a portion of the data used to derive the constants for the organic chlorides and nitriles is reproduced in Table II. Experimental data are listed in column 3 and calculated values from eq 2 are listed in column 4. Also included for comparison are estimates by other methods (columns 5 and 6; see below).

Calculations of ΔH_v for compounds such as 2-chloro-2-methylpropane and 1-cyanobicyclo[2.1.0]pentane with the aid of eq 2 require some additional comments. Both these materials contain a tertiary carbon atom that also bears the functional group in question. The shape of these molecules closely resembles the shape of the related hydrocarbon containing a quaternary carbon atom. Examination of the experimental vaporization enthalpies of these molecules confirms the general trend observed with hydrocarbons of similar structure; these molecules generally exhibit lower ΔH_v values than their linear counterparts. In calculating ΔH_v for these and related molecules, we have treated the tertiary carbon atom bearing the substituent as a quaternary carbon atom in eq 2.

Experimental data reported for the alkyl halides in Table II are typical of the results observed with most functional groups. The effect of moving a substituent from a primary position to a secondary position generally results in an experimental enthalpy of vaporization that decreases a few percent relative to the normal derivative. Branching at the α position relative to the position of the functional group has a similar effect as observed with 1-chloro-2-methylpropane. Since we have previously shown that with the exception of quaternary carbons, branching at carbon does not significantly affect the observed heat of vapori-

zation of hydrocarbons, we conclude that the effect of branching is mainly to attenuate the effectiveness of the functional group in solvation. Consistent with this interpretation is the observation that cyclic ethers, cyclic ketones, and sulfides, where the alkyl groups are tied back, generally give larger vaporization energies than estimated (see supplementary tables). Modification of the intercept, b, of eq 2 to account for structural variations can improve the correlations observed, but only at the expense of introducing additional parameters. Since these effects in most instances are relatively small, we have chosen to ignore them at present.

Also included in Table II are comparisons of ΔH_v estimates as obtained by other methods. Semiempirical estimates as calculated and compiled by Dreisbach[6] and values calculated from the group additivity table reported by Guthrie and Taylor[10,17] are listed in columns 5 and 6, respectively, if available. As noted above, agreement between experiment and the estimates obtained from eq 2 demonstrates the general applicability of eq 2. This has been achieved without sacrificing accuracy. As the size of the hydrocarbon portion of the molecule increases, the calculated values in columns 5 and 6 appear to diverge from the experimental value. Divergence of the values reported by Dreisbach may reflect the difficulty of obtaining or estimating the critical constants and other necessary parameters for materials of low volatility. This is pure speculation on our part, since we have no way of knowing to what extent experimental data were used in these estimations. With regard to the group additivity method of Guthrie and Taylor, it is clear that for linear molecules, some divergence between estimates of ΔH_v obtained from group additivity parameters and eq 2 will be observed. The origin of this divergence can be traced to the weighted differences attributed to each incremental methylene group; 1.12 by eq 2, compared to 1.21 kcal/mol for each $CH_2(C)_2$ from Guthrie.[10] Judging from the way we have derived our constants (see discussion above) and

(17) It should be noted that the group additivity parameters[10] and the constants b of Table I were derived from essentially the same data base.
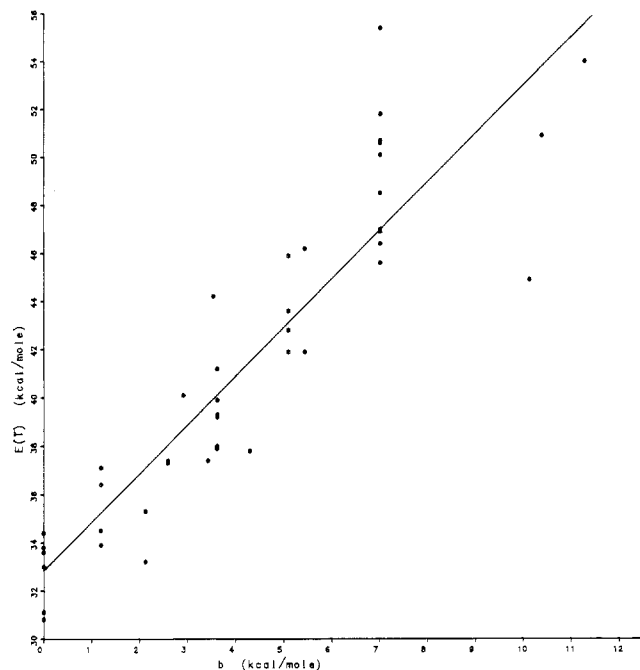
Figure 2. $E(T)$ values vs b.

from the trend observed in Table II, we would suggest that calculations using the group additivity parameters of Guthrie and Taylor will give better results for small molecules and our eq 2 will fit the larger linear molecules better. This remains to be tested.

The magnitude of the constants derived from this correlation is also of interest. Each value of b is a measure of the attractive interactions of the functional group from which it has been derived. The magnitude of b for alcohols, for example, when corrected for the contribution of the C–O bond ((b[ethers])/2), 0.6, results in a value of 6.4 kcal/mol, in good agreement with the value often used for hydrogen bonding.[9] Correlation of b with group properties of different classes of solvents seems promising since the magnitude of b should quantitatively reflect the contributions of both polar and nonpolar interactions of the functional group. For comparison, the magnitude of b for each functional group, corrected for the contributions of carbon, when necessary,[19] is summarized in Table III. Also included in Table III are characteristic E_T values, often used as a measure of solvent polarity.[18] Figure 2, illustrates the correlation observed between these two physical constants. The equation for the best fit straight line by least squares in the figure is given by

$$E_T = 2.0195\Delta H_v + 32.93 \qquad (5)$$

with a correlation coefficient of 0.9074. Agreement, although qualitative, is as good as might be expected since the magnitude of b depends on both polar and nonpolar attractive interactions of the functional group. This point is made clear by comparing the E_T and b values for chloro-, bromo-, and iodobenzene. Although the E_T values for these molecules are very similar, the value for b increases as the van der Waals size of the functional group increases.

Table III. Functional Group Contributions to Vaporization Enthalpies and E_T Values

functional group	contrib to ΔH_v,[19] kcal/mol	E_T scale, kcal/mol
–OH	7.02	45.7, 3-pentanol; 46.5, 2-pentanol; 47.0, neopentyl alcohol; 47.1, 2-butanol; 48.6, 2-propanol; 50.2, 1-butanol; 50.7, propanol; 50.8, benzyl alcohol; 51.9, ethanol; 55.5, methanol
–CHO	4.20	NA[a]
–CONH–	11.28	54.1, N-methylformamide
–NH₂	3.54	44.3, aniline
–NH–	2.12	33.3, diisopropylamine; 35.4, diethylamine
–Br	3.43	37.5, bromobenzene
–CO₂H	10.39	51.0, acetic acid
–Cl	2.59	37.4, 1-chloropropane; 37.5, chlorobenzene
–CO₂–	3.62	38.1, ethyl acetate; 40.0, methyl acetate
–O–	1.19	34.0, diisopropyl ether; 34.6, diethyl ether; 36.5, 2-methyltetrahydrofuran; 37.2, anisole
–I	4.30	37.9, iodobenzene
–CO–	3.62	38.0, diisobutyl ketone; 39.3, diethyl ketone; 39.4, methyl isobutyl ketone; 41.3, acetophenone
–CN	5.10	42.0, benzonitrile; 43.7, propionitrile; 46.0, acetonitrile
–NO₂	5.44	42.0, nitrobenzene; 46.3, nitromethane
–S–	3.20	NA
–SS–	5.32	NA
–S(O)–	10.13	45.0, dimethyl sulfoxide
–SO₂–	12.67	NA
–C(O)S–	5.15	NA
–SH	3.32	NA
hydrocarbon	0.00	30.9, hexane; 31.2; cyclohexane; 33.1, mesitylene; 33.7, tert-butylbenzene; 33.9, toluene; 34.5, benzene

[a] NA = not available.

The values can also be compared to the dipole moments of chloro-, bromo-, and iodobenzene (1.7, 1.73, and 1.9 D (gas phase); 1.56, 1.51, and 1.78 D (benzene), respectively).[20]

As noted above, eq 2 has been derived from experimental heats of vaporization of hydrocarbon derivatives containing a single functional group. The value of the equations generated in Table I should also be assessed by how useful they are in estimating vaporization enthalpies for compounds containing mixed or multiple functionality. The utility of these parameters in reproducing heats of vaporization of more highly substituted compounds will be reported soon. Additional efforts in this area are also aimed at evaluating the applicability of eq 2 in conjunction with heat of fusion measurements to estimate heats of sublimation.

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(19) The contribution of carbon to the functional group is 1.12 kcal/mol. As an example, the carbonyl group would contribute 1.12 + 2.36 kcal/mol to the vaporization enthalpy.

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nitrile, 100-47-0; 1-cyanobicyclo[3.1.0]hexane, 31357-72-9; 1-cyanocyclohexene, 1855-63-6; cyanocyclohexane, 766-05-2; heptanenitrile, 629-08-3; octanenitrile, 124-12-9; decanenitrile, 1975-78-6; undecanenitrile, 2244-07-7; dodecanenitrile, 2437-25-4; tetradecanenitrile, 629-63-0.

Kinetics of Ozonation. 6. Polycyclic Aliphatic Hydrocarbons

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The reaction of ozone with norbornane, adamantane, and bicyclo[2.2.2]octane has been studied, including kinetics and product studies as well as the determination of activation parameters for the ozonation of norbornane. This work was carried out to distinguish between hydride abstraction and a concerted insertion mechanism for the ozonation of C–H bonds. Kinetically, norbornane behaves like a secondary hydrocarbon and lacks the rate acceleration expected if a carbocation intermediate were involved in a hydride abstraction mechanism. We interpret this and other results as supporting a 1,3-dipolar insertion mechanism for the reaction of ozone with C–H bonds.

Several mechanisms have been proposed for the reaction of ozone with carbon-hydrogen bonds,[1-3] including hydride abstraction,[4] hydrogen-atom abstraction,[5,6] and a concerted C–H insertion.[3,7,8] All of these routes form hydrotrioxides, 1, which are observable at low temperatures[9,10] but decompose above −40 °C to form alcohols and carbonyl compounds, as shown in Scheme I. Evidence has been presented against all three of the pathways.

We consider the evidence against the hydrogen-atom abstraction mechanism[1,4,5] to be conclusive. Evidence against a hydride abstraction mechanism,[1,5,6,9] most noteably the retention of stereochemistry in the products,[5,6,9] also appears to be sound unless tight ion pairs are involved. Although Nangia and Benson have presented thermochemical arguments against an insertion mechanism and have favored a hydride abstraction,[4] their arguments were based on very approximate relative rate data and are not consistent with the reported absolute rates.[1,11]

We have sought a system that can distinguish in a less ambiguous way between hydride abstraction and a con-
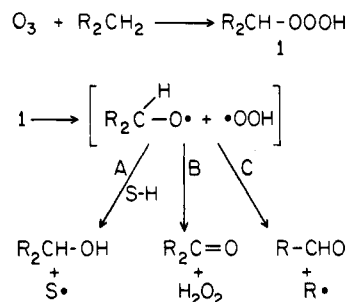
Scheme I

$$O_3 + R_2CH_2 \longrightarrow R_2CH\text{-}OOOH$$
$$1$$

$$1 \longrightarrow \left[R_2\overset{H}{\underset{}{C}}\text{-}O\cdot + \cdot OOH \right]$$

A / S–H   B   C

$$R_2CH\text{-}OH \qquad R_2C{=}O \qquad R\text{-}CHO$$
$$+ \qquad\qquad + \qquad\qquad +$$
$$S\cdot \qquad\qquad H_2O_2 \qquad\qquad R\cdot$$

Table I. Typical Product Analyses for the Reaction of Norbornane with Ozone in CCl₄[a]

% conv[b]	product ratios, %			
	norcamphor	*exo*-OH	*endo*-OH	Cl[c]
0.8	14	86	nd[d]	nd
3.1	34	62	2	2
9.6	57	37	1	5
19.2	75	17.5	0.4	7
30.6	87	5	nd	8

[a] Aliquots of 0.18 M norbornane in CCl₄ (5 mL) were bubbled with a stream of ozone at ambient temperature and were then analyzed by GC. Percentages are based on peak areas and are not corrected for relative response. [b] These values on peak areas of norbornane relative to the areas of norbornane plus products. [c] This value is for the sum of *endo*- and *exo*-2-chloronorbornane. [d] None detected.

certed insertion in the ozonation of C–H bonds. Norbornane, 2, has been reported to react with ozone 1.3 times faster than does cyclohexane, and the only products observed were *exo*-norborneol and norcamphor.[5] Due to the stability of the 2-norbornyl cation,[12,13] one would predict norbornane to exhibit higher reactivity toward ozone if a hydride abstraction mechanism were operative. Hamilton

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