An Examination of the Constancy of the CH_2 Increment in Homologous Series

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This paper deals with an evaluation of the CH_2 increment in the enthalpy of formation values of consecutive members of 11 homologous series. Literature data on enthalpies of formation of compounds in the gaseous state were examined and selected values were subjected to least-squares analyses. The following CH_2 increments were obtained (units in kJ mol^{-1}): *n*-alkanes, −20.720 ± 0.035; 2-methylalkanes, −20.973 ± 0.198; 1-cyclohexylalkanes, −20.737 ± 0.146; 1-alkenes, −20.712 ± 0.070; 1-alkanols, −20.178 ± 0.040; 2-alkanones, −20.519 ± 0.123; 1-methoxycarbonylalkanes, −20.566 ± 0.091; 1-cyanoalkanes, −20.830 ± 0.103; 1-mercaptoalkanes, −20.732 ± 0.093; 1-chloroalkanes, −21.006 ± 0.112; 1-bromoalkanes, −20.241 ± 0.118. The uncertainties given are the derived standard deviations. The value of the CH_2 increment is found to be reasonably constant within the uncertainty limits in the investigated series and identical between the series except for the 1-alkanols and the 1-bromoalkanes. The weighted mean value of the CH_2 increment, excluding those of the 1-alkanol and 1-bromoalkane series, was found to be −20.67 ± 0.05 kJ mol^{-1}.

Introduction

As early as a hundred years ago the influence of structure on energy in organic compounds was discussed by Hermann (*33*) who based his studies on combustion calorimetry measurements performed by Favre and Silberman (*14*) in the middle of the nineteenth century.

During the later half of that century Thomsen (*87*) carried out calorimetric measurements on compounds belonging to 13 homologous series, four hydrocarbon series and nine containing heteroatoms. Thomsen found that the addition of a CH_2 group to any molecule in the gaseous state resulted in an increment of its enthalpy of combustion of about 158 kcal mol^{-1} (661 kJ mol^{-1}).

In 1932 Parks and Huffman (*57*) discussed at some length linear relations between structure and energy. Two years later, Rossini (*71*) reported flame calorimetric measurements on methane, ethane, propane, *n*-butane, and *n*-pentane and included in his discussion measurements on *n*-heptane and *n*-octane by Jessup (*38*). The author stated: "In any organic molecule containing a normal alkyl group of more than 5 carbon atoms, the addition of a CH_2-group to a normal alkyl group to form the next higher normal alkyl group results in an increase in the heat of combustion of the organic molecule in the gaseous state, at the temperature of 25 °C and a constant pressure of 1 atmosphere of 157.00 ± 0.08 $kcal_{15}$ mol^{-1}" (657.12 ± 0.33 kJ mol^{-1}).

The extensive, highly accurate, combustion calorimetric work at the National Bureau of Standards, Washington, D.C., carried out in the 1930's and 1940's on hydrocarbons in this context resulted in a paper from 1946 by Prosen, Johnson, and Rossini (*63*) on the constancy of the CH_2 increment within hydrocarbon series. They suggested, on the basis of measurements on the *n*-alkane, 1-cyclopentylalkane, 1-cyclohexylalkane, 1-alkene, and 1-phenylalkane series, the following relation:

$$\Delta H_f^\circ\{\text{Y-(CH}_2)_m\text{-H,g}\}/\text{kJ mol}^{-1} = A + Bm + \delta \qquad (1)$$

where "*A* is a constant peculiar to the end group, Y; *B* is a constant for all normal alkyl series, independent of Y; and δ is a term which has a small finite value for lower members, being largest for $m = 0$, and becomes zero for higher members, beginning near $m = 4$". (Note: In eq 1 from ref 63, the end group for *n*-alkanes was the methyl group, Y = CH_3. Everywhere else in the present paper Y = H for the *n*-alkanes; cf. Table XII.) The value of the constant *B*, the CH_2 increment, was found to be −20.610 kJ mol^{-1} in the *n*-alkane series (*64*) and comparison with successive increments of the other series indicated consistency also in these.

In 1970, Cox and Pilcher (*6*) tested the relation on homologous series containing heteroatoms. From their collection of data, they found reliable experimental data for at least seven members of each of the 1-alkanol, 1-mercaptoalkane, and 1-bromoalkane series. By least-squares analyses of the data they obtained the following results: $\Delta H_f^\circ\{\text{HO-(CH}_2)_m\text{-H,g}\}/\text{kJ mol}^{-1} = -194.284 - 20.267m$, $\Delta H_f^\circ\{\text{HS-(CH}_2)_m\text{-H,g}\}/\text{kJ mol}^{-1} = -5.552 - 20.640m$, $\Delta H_f^\circ\{\text{Br-(CH}_2)_m\text{-H,g}\}/\text{kJ mol}^{-1} = -25.702 - 20.464m$.

Within the limits of error the values of *B* for the 1-mercaptoalkane and 1-bromoalkane series were unseparable from that of the *n*-alkane series (*64*) while it was doubtful if the difference in *B* for the 1-alkanol series was of statistical significance. Cox and Pilcher concluded that, for the present, it would be reasonable to assume that *B* was equal to −20.58 kJ mol^{-1} in most organic homologous series ($m \geq 3$).

In 1972, Pittam and Pilcher (*61*) reported flame-calorimetric measurements on the lower *n*-alkanes through *n*-butane. They used compounds of high purity and the derived enthalpy of formation data differed slightly from those reported in the American Petroleum Institute Research Project 44 Tables. They also reexamined the CH_2 increment in the *n*-alkane series and the value found was very close to that reported by Prosen and Rossini (*64*). Furthermore, they found that the constant δ became zero already for ethane ($m = 2$).

The scarcity of data, especially enthalpies of vaporization for compounds with eight or more carbon atoms, has led us to perform measurements on selected members of several homologous series, both energies of combustion and enthalpies of vaporization. Although many gaps still exist we have chosen at this stage to present an overall picture in regard to the following three important questions: (i) how well can the experimental results in any of the homologous series of 1-substituted straight-chain alkanes be represented by the linear relation $\Delta H_{f,i}^\circ = A_i + B_i m$ where $m \geq a$ (a = 2, 3, 4); (ii) to what extent is B_i independent of i; (iii) what is the "best" value of B_i?

The practical problem of predicting enthalpies of formation of still higher homologues as well as the formidable problem of working out precise prediction equations for branched alkanes, including mono- to polysubstituted species, undoubtedly comes down to how well we can describe the most simple case—the 1-substituted straight-chain alkanes. In this study we have

0021-9568/78/1723-0250$01.00/0

collected available data of 11 homologous series: *n*-alkanes, 2-methylalkanes, 1-cyclohexylalkanes, 1-alkenes, 1-alkanols, 2-alkanones, 1-methoxycarbonylalkanes, 1-cyanoalkanes, 1-mercaptoalkanes, 1-chloroalkanes, and 1-bromoalkanes.

All experimental determinations published since 1970, which we have found, were examined in much the same way as Cox and Pilcher did in their compilation (ref 61, p 128). A particular result was excluded for one or more of the following reasons: (1) insufficient information was given to allow reliable recalculations, (2) less than three measurements were performed, (3) the experimental precision was considerably less than that generally experienced, (4) the result was found to be incompatible with the bulk of results for the same homologous series (*72*).

Only series for which data were available for at least five members have been included (1-cyclopentylalkanes and 1-phenylalkanes have been excluded for this reason).

Calorimetric determinations of the enthalpies of vaporization were preferred to results derived from measurements of vapor pressure as a function of temperature (cf. ref 45).

Calculations

All numerical results were recalculated to the 1975 table of atomic weights (*5*). The given $\Delta H_c°$ values refer to the combustion reaction taking place at 298.15 K and 101.325 kPa with the following combustion products (whenever applicable): CO_2(g), H_2O(l), [1 mol of H_2SO_4 in 115 mol of H_2O](l), [1 mol of HCl in 600 mol of H_2O](l), and Br_2(l). In the corrections of $\Delta H_r°$ to $\Delta H_f°$ the following auxiliary data were used ($\Delta H_f°$ in kJ mol^{-1}): CO_2(g), $\Delta H_f° = -393.51 \pm 0.13$ (*4*); H_2O(l), −285.83 ± 0.042 (*4*); [1 mol of H_2SO_4 in 115 mol of H_2O](l), −887.81 ± 0.40 (*92*); [1 mol of HCl in 600 mol of H_2O](l), −166.62 ± 0.13 (*92*); HCl(g), −92.31 ± 0.13 (*4*); HBr(g), −36.38 ± 0.18 (*4*).

Other data required in calculations of enthalpies of formation from hydrogenation and equilibrium studies are specified in connection with the reaction concerned.

The $\Delta H_f°$ values refer to the hypothetical reaction taking place at 298.15 K and 101.325 kPa with all reactants and products in their thermodynamic standard states. The overall standard deviation is calculated as recommended by Rossini (*72*). In the evaluation of the constants *A* and *B* in eq 1, least-squares analysis with individual values weighted inversely as the squares of the experimental uncertainty intervals defined as twice the overall standard deviation was used. The standard error of the estimate, s_e,

$$s_e = \{\Sigma(\Delta H_f°(\text{obsd}) - \Delta H_f°(\text{calcd}))^2/(n-2)\}^{1/2}$$

n being the number of input data, was also recorded for each series.

Selected Values and Derived Results

The selected literature data have been summarized in Tables I–XI.

A survey of all compounds belonging to the 11 studied series, for which enthalpy of formation data are available, is found in Table XII.

The results of the least-squares analyses are given in Table XIII.

Discussion

A comparison has been made between all the experimental values and those calculated using the constants given in Table XIII. The differences exceeded the uncertainty interval associated with the experimental values in 12 cases out of a total of 123 and in only two of these by more than 25%.

Table I. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous *n*-Alkanes

Compound	Ref	Method[a]	$\Delta H_c°$/kJ mol^{-1}	State	$\Delta H_v°$/kJ mol^{-1}	Ref	$\Delta H_f°$(g)/kJ mol^{-1}
Ethane	73	FC	−1559.81 ± 0.46	g			−84.70 ± 0.54
	61	FC	−1560.69 ± 0.25	g			−83.82 ± 0.29
Propane	73	FC	−2219.85 ± 0.50	g			−104.00 ± 0.66
	61	FC	−2219.16 ± 0.46	g			−104.69 ± 0.63
n-Butane	65	FC	−2876.08 ± 0.63	g			−127.11 ± 0.84
	61	FC	−2877.53 ± 0.43	g			−125.66 ± 0.70
n-Pentane	73	FC	−3536.53 ± 0.88	g			−146.00 ± 1.12
	60	FC	−3535.43 ± 0.96	g			−147.10 ± 1.19
	66	SB	−3509.15 ± 0.77	l	26.74 ± 0.21	56	−146.63 ± 1.06
	22	SB	−3509.06 ± 0.67	l			−146.73 ± 0.99
n-Hexane	38	SB	−4163.74 ± 1.38	l	31.55 ± 0.04	56	−166.6 ± 1.6
	66	SB	−4163.04 ± 0.83	l			−167.28 ± 1.18
	23	SB	−4163.20 ± 0.54	l			−167.15 ± 0.98
n-Heptane	38	SB	−4816.39 ± 1.88	l	36.57 ± 0.04	56	−188.3 ± 2.1
	66	SB	−4817.15 ± 0.87	l			−187.50 ± 1.30
	7	SB	−4816.85 ± 1.46	l			−187.8 ± 1.8
n-Octane	38	SB	−5470.06 ± 1.42	l	41.15 ± 0.04[b]	56, 89	−209.0 ± 1.8
	66	SB	−5470.73 ± 1.05	l			−208.3 ± 1.5
	24	SB	−5470.27 ± 1.63	l			−208.8 ± 2.0
n-Nonane	38	SB	−6123.98 ± 1.88	l	46.44 ± 0.04	56	−229.5 ± 2.3
	66	SB	−6124.91 ± 1.12	l			−228.5 ± 1.7
	25	SB	−6125.08 ± 0.54	l			−228.37 ± 1.36
n-Decane	38	SB	−6778.19 ± 1.13	l	51.36 ± 0.04[b]	56, 89	−249.7 ± 1.8
	66	SB	−6778.59 ± 1.52	l			−249.3 ± 2.1
n-Undecane	38	SB	−7431.30 ± 2.55	l	56.43 ± 0.08	89	−270.8 ± 3.0
n-Dodecane	38	SB	−8088.56 ± 3.14	l	61.30 ± 0.25	50	−288.1 ± 3.6
	66	SB	−8086.54 ± 1.65	l			−290.1 ± 2.4
n-Hexadecane	66	SB	−10700.85 ± 2.80	l	81.38 ± 0.33	50	−373.0 ± 3.6
	21	SB	−10699.10 ± 1.76	l			−374.8 ± 2.8
	69	SB	−10698.84 ± 4.06	l			−375.1 ± 4.6

[a] Abbreviations used: FC = flame calorimetry, SB = static-bomb calorimetry, RB = rotating-bomb calorimetry, H = hydrogenation, EQ = equilibrium studies. [b] Weighted mean values.

Table II. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 2-Methylalkanes

Compound	Ref	Method[a]	ΔH_c°/kJ mol^{-1}	State	ΔH_v°/kJ mol^{-1}	Ref	ΔH_f°(g)/kJ mol^{-1}
2-Methylbutane	42	FC	−3528.69 ± 0.62	g			−153.84 ± 0.93
	60	FC	−3528.40 ± 0.92	g			−154.13 ± 1.15
	22	SB	−3504.38 ± 0.84	l	25.23 ± 0.21	75	−152.94 ± 1.11
2-Methylpentane	67	SB	−4157.21 ± 0.92	l	29.87 ± 0.04	56, 88	−174.79 ± 1.24
2-Methylhexane	7	SB	−4811.60 ± 0.96	l	34.85 ± 0.21	20	−194.76 ± 1.38
2-Methylheptane	68	SB	−5465.50 ± 1.42	l	39.66 ± 0.04	56	−215.4 ± 1.8
2-Methylnonane	49	SB	−6769.74 ± 2.34	l	48.73 ± 0.10	81	−260.8 ± 2.7

[a] See table I.

Table III. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Cyclohexylalkanes

Compound	Ref	Method[a]	ΔH_c°/kJ mol^{-1}	State	ΔH_v°/kJ mol^{-1}	Ref	ΔH_f°(g)/kJ mol^{-1}
Cyclohexylethane	39	SB	−5222.58 ± 1.46	l	40.46 ± 0.04	56	−171.7 ± 1.8
1-Cyclohexylpropane	39	SB	−5875.74 ± 1.15	l	45.10 ± 0.04	56	−193.2 ± 1.7
	26	SB	−5876.58 ± 0.92	l			−192.4 ± 1.5
1-Cyclohexylbutane	39	SB	−6530.28 ± 1.22	l	50.04 ± 0.21	16	−213.08 ± 1.84
1-Cvclohexyldecane	21	SB	−10451.18 ± 1.80	l	78.78 ± 0.42	16	−339.5 ± 2.9
	44	SB	−10451.05 ± 3.33	l			−339.6 ± 4.0
1-Cyclohexyldodecane	49	SB	−11760.26 ± 3.51	l	93.43 ± 1.26	58	−374.4 ± 4.5

[a] See table I.

Table IV. Selected Experimental Enthalpies of Reaction and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Alkenes

Compound	Ref.	Method[e]	ΔH_r°/kJ mol^{-1}	State	ΔH_v°/kJ mol^{-1}	Ref	ΔH_f°(g)/kJ mol^{-1}
1-Butene	40	H	−125.94 ± 0.42[a]	g			+0.31 ± 0.68
	65	FC	−2716.79 ± 0.75	g			−0.57 ± 0.93
1-Pentene	12	EQ[f]	−10.88 ± 0.84[b]	g			−22.30 ± 1.35
1-Hexene	18	H	−125.94 ± 1.05[c]	l	30.71 ± 0.21	19	−42.01 ± 1.27
	79	H	−126.36 ± 0.84[c]	l			−41.59 ± 1.10
1-Heptene	70	SB	−4658.32 ± 1.17	l	35.64 ± 0.17	19	−61.1 ± 1.5
	41	H	−125.06 ± 0.25[d]	g			−62.69 ± 0.97
1-Octene	70	SB	−5312.90 ± 1.13	l	40.27 ± 0.20	45	−81.6 ± 1.6
1-Decene	70	SB	−6619.56 ± 1.84	l	50.43 ± 0.20	45	−123.4 ± 2.3
1-Dodecene	82	RB	−7925.75 ± 1.33	l	60.78 ± 0.29	45	−165.6 ± 2.1
1-Hexadecene	50	SB	−10540.16 ± 1.84	l	80.25 ± 0.45	45	−249.0 ± 2.9
	82	RB	−10538.81 ± 2.02	l			−250.3 ± 3.0

[a] Refers to the reaction 1-C_4H_8(g) + H_2(g) = *n*-C_4H_{10}(g); ΔH_f°(*n*-C_4H_{10},g) = −126.25 ± 0.54 kJ mol^{-1} (*61*). [b] Refers to the reaction 1-C_5H_{10}(g) $\rightleftarrows$ *trans*-2-C_5H_{10}; ΔH_f°(*trans*-2-C_5H_{10},g) = −33.18 ± 1.05 kJ mol^{-1} (*6*). [c] Refers to the reaction 1-C_6H_{12}(l) + H_2(g) = *n*-C_6H_{14}(l); ΔH_f°(*n*-C_6H_{14},l) = −198.66 ± 0.68 kJ mol^{-1}. Weighted mean value derived from numbers given in Table I. [d] Refers to the reaction 1-C_7H_{14}(g) + H_2(g) = *n*-C_7H_{16}(g); ΔH_f°(*n*-C_7H_{16},g) = −187.75 ± 0.94 kJ mol^{-1}. Weighted mean value derived from numbers given in Table I. [e] See Table I. [f] Second law.

Table V. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Alkanols

Compound	Ref	Method[c]	ΔH_c°/kJ mol^{-1}	State	ΔH_v°/kJ mol^{-1}	Ref	ΔH_f°(g)/kJ mol^{-1}
Ethanol	74	FC	−1409.21 ± 0.25	g			−235.30 ± 0.38
1-Propanol	52	SB	−2021.19 ± 0.25	l	47.47 ± 0.02[a]	28, 48, 62, 90	−255.19 ± 0.49
1-Butanol	80	SB	−2674.86 ± 0.84	l	52.33 ± 0.04[a]	62, 90	−276.00 ± 1.01
	29	SB	−2676.43 ± 0.45	l			−274.43 ± 0.72
	10	SB	−2676.13 ± 0.24	l			−274.73 ± 0.61
1-Pentanol	30	SB	−3329.95 ± 0.64	l	56.94 ± 0.18	90	−295.64 ± 0.96
	32	SB	−3329.86 ± 0.67	l			−295.78 ± 0.98
	53	SB	−3330.86 ± 0.28	l			−294.73 ± 0.77
1-Hexanol	53	SB	−3984.32 ± 0.44	l	61.72 ± 0.12[a]	45, 90	−315.83 ± 0.95
1-Heptanol	32	SB	−4637.98 ± 0.79	l	66.81 ± 0.20	45	−336.42 ± 1.27
	53	SB	−4637.7 ± 0.5	l			−336.7 ± 1.1
1-Octanol	30	SB	−5292.47 ± 0.97	l	71.04 ± 0.48	45	−357.0 ± 1.6
	53	SB	−5293.9 ± 0.6	l			−355.6 ± 1.4
1-Nonanol	32	SB	−5946.94 ± 1.05	l	76.86 ± 0.75	45	−376.1 ± 1.8
	53	SB	−5946.2 ± 0.6	l			−376.8 ± 1.6
1-Decanol	53	SB	−6601.0 ± 1.1	l	81.59 ± 0.76	45	−396.6 ± 1.9
1-Dodecanol	53	SB	−7909.3 ± 0.8	l	91.96 ± 0.60	45	−436.7 ± 1.9
1-Tetradecanol	53	SB	−9161.9 ± 0.6	c	150.29 ± 2.09[b]	45	−479.4 ± 2.9
1-Hexadecanol	30	SB	−10468.20 ± 1.73	c	169.4 ± 2.1[b]	9	−517.6 ± 3.5
	53	SB	−10468.8 ± 0.7	c			−517.1 ± 3.1
	69	SB	−10471.7 ± 3.8	c			−513.9 ± 4.8

[a] Weighted mean values. [b] Refers to the process solid = gas. [c] See Table I.

In the paper concerning the CH_2 increment in the *n*-alkane series, Prosen and Rossini (*64*) took $m = 5$ as starting point, whereas Pittam and Pilcher (*61*) later showed that it could be taken as $m = 2$. Cox and Pilcher (*6*) tested the relations on

Table VI. Selected Experimental Enthalpies of Reaction and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 2-Alkanones

Compound	Ref	Method[c]	$\Delta H_\mathrm{r}^\circ$/kJ mol^{-1}	State	$\Delta H_\mathrm{v}^\circ$/kJ mol^{-1}	Ref	$\Delta H_\mathrm{f}^\circ$(g)/kJ mol^{-1}
Methyl ethyl ketone	11	H	54.27 ± 0.42[a]	g			−238.53 ± 1.05
	78	SB	−2443.94 ± 1.15	l	34.89 ± 0.04	54	−238.53 ± 1.27
	3	EQ[d]	54.18 ± 0.67[b]	g			−238.62 ± 1.17
Methyl *n*-propyl ketone	31	SB	−3099.39 ± 1.01	l	38.24 ± 0.21	54	−259.06 ± 1.24
Methyl *n*-butyl ketone	31	SB	−3754.00 ± 0.96	l	42.22 ± 0.08	31	−279.82 ± 1.27
Methyl *n*-heptyl ketone	77	RB	−5716.73 ± 1.23	l	56.44 ± 0.13	77	−340.9 ± 1.7
Methyl *n*-decyl ketone	77	RB	−6775.84 ± 1.71	l	73.30 ± 0.46	77	−402.9 ± 2.4

[a] Refers to the reaction $CH_3C(=O)CH_2CH_3(g) + H_2(g) \rightarrow (CH_3)_3COH$ (g) $\Delta H_\mathrm{f}^\circ$(*sec*-butyl alcohol,g) = −292.80 ± 0.96 kJ mol^{-1} (*80*). [b] Refers to the reaction $CH_3C(=O)CH_2CH_3(g) + H_2(g) \rightleftharpoons (CH_3)_3COH$ (g); $\Delta H_\mathrm{f}^\circ$(*sec*-butyl alcohol,g) = −292.80 ± 0.96 kJ mol^{-1} (*80*). [c] See Table I. [d] Second law.

Table VII. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Methoxycarbonylalkanes

Compound	Ref	Method[a]	$\Delta H_\mathrm{c}^\circ$/kJ mol^{-1}	State	$\Delta H_\mathrm{v}^\circ$/kJ mol^{-1}	Ref	$\Delta H_\mathrm{f}^\circ$(g)/kJ mol^{-1}
Methyl pentanoate	1	SB	−3561.79 ± 0.59	l	43.10 ± 0.06	45	−471.15 ± 1.01
Methyl hexanoate	1	SB	−4215.11 ± 0.92	l	48.04 ± 0.12	45	−492.23 ± 1.33
Methyl heptanoate	1	SB	−4867.55 ± 0.79	l	51.62 ± 0.48	45	−515.55 ± 1.43
Methyl octanoate	1	SB	−5523.67 ± 0.79	l	56.41 ± 0.50	45	−534.0 ± 1.5
Methyl nonanoate	1	SB	−6177.07 ± 1.51	l	61.99 ± 0.41	45	−554.3 ± 2.1
Methyl decanoate	1	SB	−6832.10 ± 1.72	l	66.75 ± 0.57	45	−573.9 ± 2.4
Methyl undecanoate	1	SB	−7486.76 ± 1.30	l	71.37 ± 0.30	45	−594.0 ± 2.1
Methyl dodecanoate	1	SB	−8138.24 ± 1.59	l	77.17 ± 0.56	45	−616.0 ± 2.4
Methyl tridecanoate	1	SB	−8792.64 ± 1.80	l	82.68 ± 0.84	45	−635.4 ± 2.8
Methyl tetradecanoate	1	SB	−9446.00 ± 2.09	l	86.98 ± 0.94	45	−657.1 ± 3.1
Methyl pentadecanoate	1	SB	−10098.28 ± 1.51	l	93.49 ± 0.94	45	−677.7 ± 2.8

[a] See Table I.

Table VIII. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Cyanoalkanes

Compound	Ref	Method[a]	$\Delta H_\mathrm{c}^\circ$/kJ mol^{-1}	State	$\Delta H_\mathrm{v}^\circ$/kJ mol^{-1}	Ref	$\Delta H_\mathrm{f}^\circ$(g)/kJ mol^{-1}
Butanenitrile	13	SB	−2568.77 ± 0.92	l	39.33 ± 0.08	34	33.65 ± 1.05
Pentanenitrile	43	SB	−3220.59 ± 1.30	l	43.60 ± 0.10	34	10.41 ± 1.47
Octanenitrile	83	RB	−5184.49 ± 0.97	l	56.80 ± 0.27	83	−50.5 ± 1.5
Decanenitrile	83	RB	−6492.13 ± 1.16	l	66.84 ± 0.37	83	−91.5 ± 1.8
Undecanenitrile	83	RB	−7145.34 ± 1.29	l	71.14 ± 0.14	83	−113.5 ± 2.0
Tetradecanenitrile	83	RB	−9107.78 ± 1.79	l	85.29 ± 0.51	83	−174.8 ± 2.7

[a] See Table I.

Table IX. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Mercaptoalkanes

Compound	Ref	Method[a]	$\Delta H_\mathrm{c}^\circ$/kJ mol^{-1}	State	$\Delta H_\mathrm{v}^\circ$/kJ mol^{-1}	Ref	$\Delta H_\mathrm{f}^\circ$(g)/kJ mol^{-1}
Mercaptoethane	46	RB	−2173.01 ± 0.42	l	27.32 ± 0.04	47	−46.16 ± 0.66
1-Mercaptopropane	35	RB	−2826.11 ± 0.46	l	32.01 ± 0.08	59	−67.72 ± 0.75
1-Mercaptobutane	36	RB	−3480.63 ± 1.09	l	36.57 ± 0.08	76	−87.97 ± 1.29
1-Mercaptopentane	37	RB	−4132.52 ± 1.59	l	41.13 ± 0.08	15	−110.9 ± 1.8
	86	RB	−4133.61 ± 0.67	l			−109.77 ± 1.05
1-Mercaptohexane	27	RB	−4788.60 ± 0.75	l	45.77 ± 0.21	55	−129.48 ± 1.21
1-Mercaptoheptane	27	RB	−5442.87 ± 0.75	l	50.58 ± 0.21	55	−149.73 ± 1.30
1-Mercaptodecane	27	RB	−7404.50 ± 1.21	l	65.48 ± 0.54	45	−211.2 ± 2.0

[a] See Table I.

Table X. Selected Experimental Enthalpies of Reaction and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Chloroalkanes

Compound	Ref	Method[a]	$\Delta H_\mathrm{r}^\circ$/kJ mol^{-1}	State	$\Delta H_\mathrm{v}^\circ$/kJ mol^{-1}	Ref	$\Delta H_\mathrm{f}^\circ$(g)/kJ mol^{-1}
Chloroethane	17	FC	−1413.05 ± 0.59	g			−112.25 ± 0.66
1-Chloropropane	8	H	−65.81 ± 0.67[b]	g			−130.86 ± 0.82
	17	FC	−2072.09 ± 0.79	g			−132.55 ± 0.90
1-Chlorobutane	84	RB	−2695.80 ± 1.12	l	33.52 ± 0.06	91	−154.66 ± 1.25[c]
1-Chloropentane	84	RB	−3349.85 ± 1.20	l	38.24 ± 0.02	91	−175.23 ± 1.39[c]
1-Chlorooctane	84	RB	−5309.98 ± 1.83	l	52.42 ± 0.12	91	−238.9 ± 2.1[c]
1-Chlorododecane	84	RB	−7926.30 ± 2.35	l	71.93 ± 0.32	45	−320.5 ± 2.9[c]

[a] See Table I. [b] Refers to the reaction 1-$C_3H_7Br(g) + H_2(g) = C_3H_8(g) + HCl(g)$; $\Delta H_\mathrm{f}^\circ(C_3H_8,g)$ = −104.36 ± 0.46 kJ mol^{-1} (*61*) and $\Delta H_\mathrm{f}^\circ$(HCl,g) = −92.31 ± 0.13 kJ mol^{-1} (*4*). [c] The given uncertainties differ slightly from those given in the original paper due to an erroneous treatment of the experimental uncertainties of carbon dioxide and water.

series containing a heteroatom and started with $m = 4$. The starting point in most of the series in the present calculations was $m = 2$ (no significant improvement in the fit was found when the least-squares analyses started with $m = 3$ or $m = 4$)

Table XI. Selected Experimental Enthalpies of Combustion and Vaporization and Derived Enthalpies of Formation at 298.15 K of Gaseous 1-Bromoalkanes

Compound	Ref	Method[a]	$\Delta H_c°$/kJ mol^{-1}	State	$\Delta H_v°$/kJ mol^{-1}	Ref	$\Delta H_f°$(g)/kJ mol^{-1}
1-Bromobutane	2	RB	−2716.38 ± 1.26	1	36.60 ± 0.10	91	−107.30 ± 1.38
1-Bromopentane	2	RB	−3369.28 ± 1.42	1	41.43 ± 0.03	91	−128.9 ± 1.6
1-Bromohexane	2	RB	−4024.55 ± 1.59	1	46.12 ± 0.10	91	−148.3 ± 1.8
1-Bromoheptane	2	RB	−4679.66 ± 1.59	1	50.79 ± 0.10	91	−167.8 ± 1.9
1-Bromooctane	2	RB	−5332.39 ± 2.26	1	55.77 ± 0.13	45	−189.5 ± 2.5
1-Bromododecane	85	RB	−7950.21 ± 1.97	1	74.77 ± 0.38	45	−270.0 ± 2.6
1-Bromohexadecane	85	RB	−10567.73 ± 1.72	1	94.43 ± 1.51	45	−350.2 ± 3.2

[a] See Table I.

Table XII. Summary of Compounds Included in the Calculations[a]

	Number of carbon atoms in the *n*-alkyl chain														
End group	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Hydrogen	∇	∇	∇	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C				∇C
Isopropyl	∇C	∇C	∇C	∇C		∇C									
Cyclohexyl	∇C	∇C	∇V						∇V		∇V				
Vinyl	Σ	Σ	ΣV	ΣV	∇C		∇C		∇C				∇C		
Hydroxy	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C		∇C		∇C		∇V
Acetyl	ΣC	∇C	∇C			∇C			∇C						
Methoxycarbonyl			∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C	∇C		
Cyano		∇C	∇C			∇C		∇C	∇C			∇C			
Mercapto	∇C	∇C	∇C	∇C	∇V	∇V			∇C						
Chloro	∇	Σ	∇C	∇C			∇C				∇C				
Bromo			∇C	∇C	∇C	∇C	∇C				∇C				∇C

[a] Enthalpy of reaction: ∇ = combustion calorimetry; Σ = combustion calorimetry and/or other methods. Enthalpy of vaporization: C = calorimetric; V = vapor pressure.

Table XIII. Results of the Least-Squares Analyses

Homologous series	No. of compd/ no. of input data	A	s_A	B	s_B	s_e
n-Alkane	12/30	−42.65	0.16	−20.720	0.035	1.24
2-Methylalkane	5/7	−111.62	0.60	−20.973	0.198	1.30
1-Cyclohexylalkane	5/7	−130.44	0.71	−20.737	0.146	1.23
1-Alkene	8/12	+41.30	0.33	−20.712	0.070	1.25
1-Alkanol	12/21	−194.64	0.20	−20.178	0.040	1.24
2-Alkanone	5/7	−197.54	0.47	−20.519	0.123	0.22
1-Methoxycarbonylalkane	11/11	−389.72	0.68	−20.556	0.091	1.39
1-Cyanoalkane	6/6	+95.39	0.68	−20.830	0.103	1.41
1-Mercaptoalkane	7/8	−5.20	0.41	−20.732	0.093	1.52
1-Chloroalkane	6/7	−69.58	0.41	−21.006	0.112	2.35
1-Bromoalkane	7/7	−26.83	0.85	−20.241	0.118	0.74

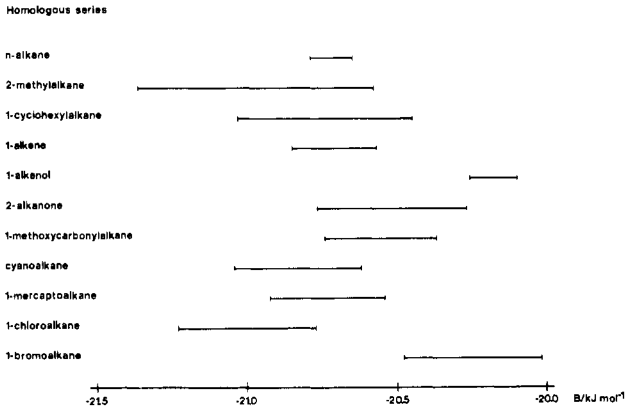

Figure 1. The CH_2 increments of 11 homologous series given with twice the calculated standard deviation.

exceptions being the 1-bromoalkane series, where large scatter in the reported values for bromoethane and 1-bromopropane forced us to start with *m* = 4, the cyanoalkanes with *m* = 3, and the 1-methoxycarbonylalkanes with *m* = 4 for which no results are available for lower *m* values.

The derived CH_2 increments with twice the calculated standard deviations are shown in Figure 1. As can be seen, with the exception of the 1-alkanol and the 1-bromoalkane series, the intervals overlap. It is surprising that the 2-methylalkanes show such a large spread and a value of *B* which deviates considerably from that for the *n*-alkane series. Exclusion of 2-methylnonane gives *B* = −20.606 ± 0.254, in much better agreement with the *n*-alkanes (but then only four compounds in the series remain), indicating that a redetermination of the enthalpy of formation of this compound should be made.

The discrepancy in the 1-alkanol series is of particular interest and the series has been subjected to a special analysis. It has been suggested that the discrepancy could be caused by the highly polar OH group interacting with the neighboring carbon atoms, and thus the CH_2 increment would gradually approach a "normal value" with larger chain length. This has been tested by a least-squares analysis beginning with *m* = 2, *m* = 3, and so on. Figure 2 shows the derived CH_2 increments for starting points *m* = 2 through *m* = 9. The shape convincingly proves that an explanation must be sought elsewhere. Another possible reason for the discrepancy might be the presence of severe systematic errors in the experimental data, i.e., in enthalpies of combustion or vaporization. The many independent determinations of enthalpies of combustion giving results of satisfactory agreement exclude the presence of systematic errors. The determinations of enthalpy of vaporization data are less numerous and the majority used in this investigation come from our laboratory.

The 1-alkanols with 2–7 carbon atoms were determined using

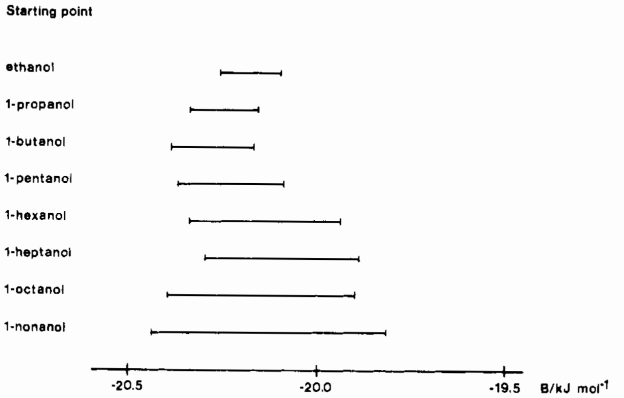

Figure 2. The CH_2 increments of the 1-alkanol series given with twice the calculated standard deviation, based on a decreasing number of species: from C_5–C_{16}, 21 data points, to C_9–C_{16}, 8 data points.

the Wadsö calorimeter (*89*) and with 8–10, 12, and 14 carbon atoms using the Morawetz calorimeter (*51*). As the CH_2 increment in the enthalpy of vaporization is constant, within uncertainty limits, whether it is calculated from all data or only from data of 1-octanol and higher members, the presence of a serious systematic error in enthalpy of vaporization data must imply that both methods are impaired by almost the same systematic relative error. All our experience indicates that this is not true.

A corresponding treatment of the 1-bromoalkane series does not reveal any similar trend. However, such an analysis is not particularly conclusive as the number of compounds studied is limited to 7 in comparison to 12 for the 1-alkanols.

The weighted mean CH_2 increment, omitting the increment of the 1-alkanol and 1-bromoalkane series, was found to be -20.67 ± 0.05 kJ mol^{-1}, where the uncertainty interval represents twice the calculated standard deviation.

For the present it would be reasonable to assume that the value of the constant B in eq 1 is -20.67 kJ mol^{-1} for most 1-substituted straight-chain alkanes. Thus the enthalpy of formation for any gaseous member with $m \geq 2$ of simple homologous series can be satisfactorily estimated provided that a reliable value for one member with $m \geq 2$ is known.

Acknowledgment

The authors are grateful to Mr. Jan Rise, Department of Mathematical Statistics, University of Lund, for many valuable discussions concerning the treatment of numerical data.

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Received for review October 17, 1977. Accepted March 24, 1978. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

NEW COMPOUNDS

Synthesis of *N*,*N*′-Diarylformamido-*N*″-arylcarbamides and -thiocarbamides and *N*-Benzoylformamido-*N*′-arylcarbamides and -thiocarbamides and Their Molybdenum(V) Chloride Complexes

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New dimeric complexes of molybdenum(V) chloride with *N*,*N*′-diarylformamido-*N*″-arylcarbamides and -thiocarbamides and *N*-benzoylformamido-*N*′-arylcarbamides and -thiocarbamides having a general formula $[MoCl_2L_2]Cl_3$ have been synthesized in chloroform solution (where L = a molecule of bidentate ligand). These complexes have been characterized on the basis of elemental analysis conductance in solution, magnetic susceptibility, and infrared spectral studies. The coordination, through sulfur and nitrogen in the case of *N*,*N*′-diarylformamido-*N*″-arylthiocarbamides and *N*-benzoylformamido-*N*″-arylthiocarbamides and through oxygen and nitrogn in the case of *N*,*N*′-diarylformamido-*N*″-arylcarbamides and *N*-benzoylformamido-*N*′-arylcarbamide, and octahedral configuration of these complexes have been proposed.

Introduction

The complex compounds of $MoCl_5$ with a number of primary, secondary, and tertiary amines were prepared by Edwards and Fowles (*4*) in benzene solution. The formation of Mo(V) and Mo(VI) complexes with 8-hydroxyquinoline-5-sulfonic acid has been reported by Spence and Peterson (*7*) and they have calculated the formation constants. Nitrogen donor ligands can produce Mo(IV) complexes with $MoCl_5$ but there are complexes where reduction does not occur. 2,4,6-Trimethylpyridine forms $MoCl_4(Me_3C_5H_2N_2)_2Cl$, for which the effective magnetic moment is 1.41 μ_B (*1*).

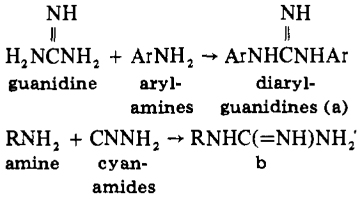
A careful survey of the literature revealed that no work has been done on the complex-forming ability of substituted formamido(N″-substituted)thiocarbamides and -carbamides. The present communication describes our studies on the synthesis of *N*,*N*′-(diaryl substituted)formamido-*N*″-arylcarbamides and -thiocarbamides and *N*-benzoylformamido-*N*′-arylcarbamides and -thiocarbamides and dimagnetic chelates of these ligands with $MoCl_5$.

Experimental Methods

All the chemicals used were either BDH "Analar" quality or E. Merck "G.R." quality. Alcohol, chloroform, and dimethylformamide were distilled before they were used.

The general method of preparation of ligands *N*,*N*-diphenylformamido-*N*″-phenylthiocarbamide (DPFPTC), *N*,*N*-diphenylformamido-*N*″-phenylcarbamide (DPFPC), *N*,*N*-diphenylformamido-*N*″-*o*-tolylthiocarbamide (DPF-*o*-TTC), *N*,-*N*-diphenylformamido-*N*″-*p*-tolylthiocarbamide (DPF-*p*-TTC), *N*-benzoylformamido-*N*′-phenylthiocarbamide (BFPTC), *N*-benzoylformamido-*N*′-phenylcarbamide (BFPC), *N*-benzoylformamido-*N*′-*o*-tolylthiocarbamide (BF-*o*-TTC), and *N*-benzoylformamido-*N*-*p*-tolylthiocarbamide (BF-*p*-TTC) is summarized as follows. The required symmetrical or asymmetrical guanidines were refluxed for 1.5 h with the appropriate aryl isocyanates or aryl isothiocyanate in 1:1 molar ratio in the alcoholic medium. After the completion of the reaction, excess alcohol was distilled out and the ligand was recovered and recrystallized from hot ethanol.

The symmetrical (a) and asymmetrical (b) guanidines have been synthesized (Sheers, E. H., "Encyclopedia of Chemical Technology" 2nd ed, Vol. 10, Wiley, New York, N.Y., 1966, pp 736, 740.) by the following reactions:



$$\underset{\text{guanidine}}{H_2N\overset{\overset{\displaystyle NH}{\|}}{C}NH_2} + \underset{\text{aryl-amines}}{ArNH_2} \rightarrow \underset{\text{diaryl-guanidines (a)}}{ArNH\overset{\overset{\displaystyle NH}{\|}}{C}NHAr}$$

$$\underset{\text{amine}}{RNH_2} + \underset{\text{cyan-amides}}{CNNH_2} \rightarrow \underset{\text{b}}{RNHC(=NH)NH_2}$$

The interaction of *N*,*N*-Diphenylguanidine (I) with aryl isocyanates and aryl isothiocyanates yields the formation of *N*,-*N*′-diarylformamido-*N*″-arylcarbamides (II) and *N*,*N*′-diarylformamido-*N*″-arylthiocarbamides (III) by the mechanism shown in Scheme I.

On the other hand asymmetrical guanidine IV leads to the formation of products V and VI with aryl isothiocyanates and aryl isocyanate, respectively (Scheme II).

Purity of these ligands was checked by sharp melting point and elemental analysis.

General Method of the Preparation of Complexes

A chloroform solution (0.1 M) of ligand was added drop by drop with constant stirring to a chloroform solution of anhydrous $MoCl_5$ (0.1 M). During the course of reaction temperature was maintained below 10 °C. After completion of the reaction, the reaction mixture was allowed to stand for an hour to attain equilibrium. The colored complexes could be separated by distilling out the excess solvent ($CHCl_3$). Melting points of these

0021-9568/78/1723-0256$01.00/0