ESTIMATION OF STANDARD ENTHALPY OF FORMATION OF ALKANES IN GASEOUS STATE BY CALCULATING SIZE, STRUCTURAL AND ELECTRONIC PARAMETERS IN THE MOLECULES.

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Abstract: A quantitative analysis is made on the correlation ship of thermodynamic property, i.e., standard enthalpy of formation (ΔH_f^0) with Kier's molecular connectivity index $(^1X^v)$, vander waal's volume (Vw) electrotopological state index (E) and refractotopological state index (R) in gaseous state of alkanes. The regression analysis reveals a significant linear correlation of standard enthalpy of formation (ΔH_f^0) with $^1X^v$, Vw, E and R. The equations obtained by regression analysis may be used to estimate standard enthalpy of formation (ΔH_f^0) of alkanes in gaseous state.

Keywords: Kier's molecular connectivity (1Xv); vander waal's volume (Vw); Electrotopological state index (E); Refractotopological state (R).

I. INTRODUCTION

Standard enthalpy of formation is a basic thermodynamic property. It is used in chemical engineering calculations. Experimental measurements of standard enthalpy of formation (ΔH_f^0) involve experimental difficulties and they are not always feasible and the corresponding methods possess real drawbacks. Consequently, it is necessary to resort to a theoretical calculation of these parameters. This option is now accessible because an important, fruitful and current field of research.

The additive approach applied to the estimation of thermo physical properties was systematically developed by S.W.Benson and co-workers[1-3]. Many topological distances based indices as molecular descriptors for QSAR[4,5] and additive scheme[6] have been developed for the estimation of enthalpy of formation of organic compounds.

One of the most important points in such research is the selection of adequate descriptors containing the information stored in the molecular structure. The quite satisfactory results of applying regression analysis may be used to calculate heats of formation seems to indicate this way is a suitable one to compute the enthalpy content of molecules. Since results are good enough and errors are nearly the same as experimental uncertainties, the equations show to be a suitable method to systematize data and to derive certain rules regarding the structural elements and group contribution to the molecular enthalpy of formation.

There are a wide variety of molecular descriptors to be used as independent variable and this large number of possibilities allows one to make quite different choices to perform the calculation

and to interpret in a meaningful way the results. In view of the above, it is thought that heat enthalpies of formation which depend upon the size, structure, electronic environment and complexity of the molecules, may be quantitatively correlated with size, structure and electronic parameters, i.e. first order valence connectivity ($^1X^v$), vander waal's volume (Vw), electrotopological state index (E) and refractotopological state (R) in alkanes. Previously we have established a significant quantitative co-relationship of these parameters with diamagnetic susceptibility of many organic compounds[7,8]. The aim of this paper is to obtain the correlation equations of (ΔH_f^0) with $^1X^v$, Vw, E and R parameters.

1. Calculation of Kier`s[9] molecular connectivity ($^1X^v$):

It is calculated by a hydrogen suppressed graph of the molecule[10]. The first order valence connectivity ($^1X^v$) is given by eq. 1:

$$^1X^v = \sum (\delta i^v . 3\delta j^v)^{-1/2} \tag{1}$$

Here the sum is the overall connections or edges in such a graph, δi^v and δj^v are numbers assigned to each atom reflecting the numbers of atoms adjacent or connected to atom (i) and (j) which are formally bonded. The atom connectivity term (δi^v)is defined as

$$\delta i^v = \frac{Zi^v - hi}{Z - Zi^v - 1} \tag{2}$$

Where Zi^v = number of valence electron of atom (i), Z = atomic number of atom (i) and hi = number of hydrogen atoms attached to atom (i).

Table (1) shows the atom connectivity (δi^v) values in different groups as calculated by eq.(2)

Table 1. Atom connectivity (δi^v) values in different groups

Groups	δi^v	Groups	δi^v
- CH$_3$	01	= CH$_2$	02
$\equiv$ CH	03	- OH	05
-NH$_2$	03	O	06
-NH -	04	C = O	06
- C $\equiv$ N	05	Furan O	06
- C = NH	04	O =N O	06
N or Pyridine N	05	H$_2$O	04
NH$_3$	02	F	(-) 20
NH$_4$	01	Cl	0.690
> N < $^+$	06	Br	0.254
= N H$_2$ $^+$	03	I	0.085

2. Calculation of vander waal's Volume (Vw):

Another atomic parameter accounting for the size of a molecule, the vander waal`s volume (Vw) may be calculated as suggested by Bond[11]. The atoms are assumed to be spherical and necessary corrections for the overlap in the hydrogen chain are also incorporated[12]

$$Vw = \sum n_i \, a_i + [\sum \text{corrections for bonds} + \sum \text{corrections for no. of branching}] \tag{3}$$

Where, Vw = vander waal's volume of the molecules

n_i = no. of atoms.

a_i = vander waal's volume of atom i.

Table 2 shows vander waal's volume of different atoms and table 3 shows correction values of vander waal's volume for sphere overlapping due to covalent bonding and for Branching. The value of vander waal's may be calculated as eq. 3.

Table 2. vander waal's volume of different atoms

Atom	Sphere volume 10^2 A$^{0\,3}$	Atom	Sphere volume 10^2 A$^{0\,3}$	Atom	Sphere volume 10^2 A$^{0\,3}$
C	0.206	H	0.056	N	0.141
O	0.115	S	0.244	F	0.115
Aliphatic Cl	0.206	Aromatic Cl	0.244	Aliphatic Br	0.244
Aromatic Br	0.287	Aliphatic I	0.335	Aromatic I	0.388

Table 3. Correction values of vander waal's volume for sphere overlapping due to covalent bonding and for Branching

Bond	Correction value 10^2 A$^{0\,3}$	Bond	Correction value 10^2 A$^{0\,3}$	Bond	Correction value 10^2 A$^{0\,3}$
C-C	-0.078	C-H	-0.043	C-N	-0.065
C-O	-0.056	C-S	-0.066	C-F	-0.056
Aliph. C-Cl	--0.058	Arom C-Cl	-0.066	Aliph. C-Br	-0.060
Arom. C-Br	-0.068	Aliph.C-I	-0.063	Arom. C-I	-0.072
C-B	-0.113	H-H	-0.030	N-H	-0.038
N-N	-0.050	N-O	-0.042	N-S	-0.061
O-H	-0.034	O-B	-0.079	S-H	-0.040
S-S	-0.062	S-F	-0.052	C=C	-0.094
C=N	-0.072	C=O	-0.068	C=S	-0.081
N=N	-0.061	N=O	-0.053	S=O	-0.057
C$\equiv$C	-0.0101	C$\equiv$N	-0.079	Arom.C=C	-0.086
Branching for Saturated bond Except bonding with H	-0.050				

3. Calculation of electrotopological state Index (E-State):

This index is developed from chemical graph theory and uses the chemical graph (hydrogen-suppressed skeleton) for generation of atom -level structure indices. This index recognizes that every atom in a molecule is unique, and this uniqueness arises from differences in the electronic and topological environment of each atom. This descriptor is formulated as an intrinsic value Ii plus a perturbation given by the electronic influence of the topological environment of the molecule[13-15]. Intrinsic state valence Ii of each atom is calculated as follow:

$$I_i = [(2/N)^2 \, \delta v + 1] / \delta \qquad (4)$$

Where N is the principal quantum number of the atom i, δv the number of valence electrons in the skeleton $(Z_v\text{-}hi)$; δ the number of σ electrons in the skeleton $(\sigma - h)$. For a skeleton, Z_v the total number of electrons on the atom . σ the number of electrons in the σ orbitals, h the number of bonded hydrogen atom. E-state for an atom i in molecule (Si) is given by

$$Si = Ii + \sum \Delta Ii \qquad (5)$$

Δ Ii = quantifies the perturbation effect on the intrinsic atom value. This perturbation is assumed to be a function of the difference in the intrinsic values Ii and Ij:

$$\Delta Ii = \sum (Ii - Ij) / r_{ij}^2 \qquad (6)$$

Where, r_{ij} is the number of atoms in the shortest path between atoms i and j including both i and j.

The difference in intrinsic values Δ Ii for a pair of skeletal atoms encode both electronic and topological attributes that arise from electro negativity differences and skeletal connectivity. Therefore, the total of sum of the differences in intrinsic values,

$\sum \Delta Ii$, due to perturbation for a whole molecule is zero i.e.. $\sum \Delta Ii = 0$ so,

$$Si = Ii \qquad (7)$$

Therefore, E- state for a molecule = $\sum ni \, Si$ or $\sum ni \, Ii \qquad (8)$

Table 4. Intrinsic state valence Ii of atoms in some groups

Group	Ii	Group	Ii	Group	Ii
> C <	1.250	>CH-	1.333	-CH$_2$ -	1.5
> C =	1.667	-S-	1.833	-CH$_3$, =CH-, > N -	2.00
-I	2.12	$\equiv$C -,-NH-	2.5	-Br	2.75
= CH$_2$, =N-	3.00	-SH	3.222	-O-	3.500
=CH, -NH$_2$	4.00	-Cl	4.111	$\equiv$N, -OH	6.00
=O	7.00	-F	8.000		

4. Calculation of refractotopological state Index (R- state):

The R state index is also developed from the chemical graph theory. This index is based on the influence of dispersive forces of each atom on the other atom in the molecule, modified by molecular topology. Crippen et al [16] reported the atomic refractivity values of the topological environment of each skeleton atom in the molecule. The evaluation of the individual atomic refractivity value (Calculated by Ghose and Crippen [16]) is based on the idea that the sum of the atomic values (αi) being related to the molecular value of the molar refractivity:

$$R \, (molecule)_{calc.} = \sum ni \, \alpha i . \qquad (9)$$

Where, ni = No. of atoms ; αi = Atomic refractivity value

Table 5. Atomic refractivity values as calculated by Ghose and Crippen used in the analysis

Atom Type	Atomic Refractivity	Atom Type	Atomic Refractivity	Atom Type	Atomic Refractivity
C (sp^3)	2.816	C(sp^2)	3.828	C(sp)	3.897
C(Ar)	3.509	C=X	3.089	H	0.916
-O-	1.635	=O	1.796	O=N	2.141
N(sp^3)	3.010	N(sp^2),N(sp)	3.201	N(Ar)	2.766
NO$_2$	3.505	Ar-N=X	3.810	F	1.063
Cl	5.611	Br	8.678	I	13.874
S(sp^3)	7.319	S(sp^2)	9.168	R-SO-R	6.076

II. RESULTS AND DISCUSSION:

The values of standard heat enthalpy of formation (ΔH_f^0) of gases are taken from literature.[17-21] Standard heat enthalpies (ΔH_f^0) are taken in kilo calories per mole at atmospheric pressure at 298.15K in gas phase. The values of $^1\chi^v$, V_w, E and R are correlated with standard heat enthalpies (ΔH_f^0).

The regression analysis reveals that the correlations of standard heat enthalpies (ΔH_f^0) with the molecular connectivity ($^1\chi^v$) & van der waals volume (V_w) show very low level of significance , but with the inclusion of indicator variable (I), i.e, I = 0 for straight chain and I = 1 for branched alkanes, shows high level of significance and are shown by equations (10) & (11).

$$\Delta H_f^0 = - 9.829 \, (\pm 0.175) \, ^1\chi^v - 4.871 \, (\pm 0.670) \, I - 11.288 \qquad (10)$$

N = 44 , r = 0.994 , s = 1.889 , F (2, 41) = 1776.123

$$\Delta H_f^0 = - 31.724 \, (\pm 0.477) \, V_w - 4.979 \, (\pm 0.574) \, I - 7.628 \qquad (11)$$

N = 45 , r = 0.996 , s = 1.711 , F (2,42) = 2362.53

Both equations show almost 100 % correlation . It shows that branching in chains plays an important role in the correlations of the molecular connectivity ($^1\chi^v$) & van der waals volume (V_w) with the standard heat enthalpies (ΔH_f^0) of the alkanes. In the equation (10) & (11), the F values are significant at 99% level [$F^2_{42} (0.01) = 5.18$] and are accounting for 98.8% & 99.2% variance ($r^2 = 0.988$ & 0.992) respectively.

The correlations of standard heat enthalpies (ΔH_f^0) with electrotopological state index (E) and refractotopological state index (R) have been given by equations (12) & (13).

$$\Delta H_f^0 = - 3.259 \, (\pm 0.023) E - 7.573 \qquad (12)$$

N = 45 , r = 0.999 , s = 0.810 , F (1, 43) = 19512.99

$$\Delta H_f^0 = - 1.033 \, (\pm 0.013) R - 11.114 \qquad (13)$$

N = 46 , r = 0.997 , s = 1.452 , F (1,44) = 6581.835

These equations show the high level of significance. Because, correlation coefficients and F value is again at 99% level [$F^1_{44} (0.01) = 7.31$] ,99.8% & 99.4%

variance ($r^2 = 0.998$ & 0.994) high.Standard deviations have minimum variation about the line of regression. All these factors show perfect correlations.

Experimental and theoretical values of standard heat enthalpies of formation (ΔH_f^0 **of** some alkanes calculated by equations (10),(11), (12) and (13) shows good agreement and are listed in tables 6. & 7.

Table 6. Experimental and theoretical calculated values of ΔHf0 by 1Xv & Vw parameters in alkanes

Name of compound	1Xv	Vw	I	ΔHf0		
				Exp.value	Cald.Eq.10	Cald.Eq.11
Methane	0.000	0.258	0	-17.890	*	-15.813
Ethane	1.000	0.412	0	-20.240	-21.117	-20.699
Propane	1.414	0.566	0	-24.820	-25.186	-25.584
n-Butane	1.914	0.720	0	-30.150	-30.100	-30.470
2-Methyl propane	1.731	0.670	1	-32.150	-33.173	-33.862
n-Pantane	2.414	0.874	0	-35.000	-35.015	-35.355
2-Methyl butane	2.269	0.824	1	-36.920	-38.461	-38.748
2,2-Dimethyl propane	2.000	0.774	1	-39.170	-35.817	-37.162
n-Hexane	2.914	1.028	0	-39.960	-39.930	-40.241
2-Methyl pentane	2.769	0.978	1	-41.660	-43.375	-43.633
3-Methyl pentane	2.807	0.978	1	-41.020	-43.749	-43.633
2,2-Dimethyl butane	2.560	0.928	1	-44.350	-41.321	-42.047
2,3-Dimethyl butane	2.641	0.928	1	-42.490	-42.107	-42.047
Heptane	3.414	1.182	0	-44.880	-44.844	-45.126
2-Meyhyl hexane	3.269	1.132	1	-46.590	-48.290	-48.519
3-Mehtyl hexane	3.307	1.132	1	-45.960	-48.663	-48.519
2,2-Dimethyl pentane	3.061	1.082	1	-49.270	-46.235	-46.933
2,3-Dimethy pentane	3.179	1.082	1	-47.620	-47.405	-46.933
2,4-Dimethyl pentane	3.124	1.082	1	-48.280	-46.865	-46.933
2,2,3-Trimethyl butane	2.942	1.032	1	-48.950	-45.076	-45.346
Octane	3.914	1.336	0	-49.820	-49.759	-50.011
2-Methyl heptane	3.769	1.286	1	-51.500	-53.204	-53.404
3-Methyl heptane	3.807	1.286	1	-50.820	-53.578	-53.404
4-Methyl heptane	3.807	1.286	1	-50.690	-53.578	-53.404
2,2-Dimethyl hexane	3.560	1.236	1	-53.710	-51.150	-51.818
2,3-Dimethyl hexane	3.679	1.236	1	-51.130	-52.320	-51.818
2,4-Dimethylhexane	3.662	1.236	1	-52.440	-52.153	-51.818
2,5-Dimethylhexane	3.624	1.236	1	-53.210	-51.779	-51.818
3,3-Dimethylhexane	3.620	1.236	1	-52.610	-51.740	-51.818
3,4-Dimethylhexane	3.717	1.236	1	-50.910	-52.693	-51.818
Nonane	4.414	1.490	0	-54.740	-54.673	-54.897
2,2,3-Trimethylpentane	3.480	1.186	1	-52.610	-50.364	-50.232
2,2,4-Trimethylpentane	3.415	1.186	1	-53.570	-49.725	-50.232
2,3,3-Trimethylpentane	3.502	1.186	1	-51.730	-50.580	-50.232
2,3,4-Trimethylpentane	3.551	1.186	1	-51.970	-51.062	-50.232
3-Ethyl pentane	3.345	1.132	1	-45.330	-49.037	-48.519

3-Methyl-3-ethyl pentane	3.680	1.236	1	-51.380	-52.329	-51.818
2-Methyl-3-ethyl pentane	3.717	1.236	1	-50.480	-52.693	-51.818
Undecane	5.414	1.798	0	-64.600	-64.502	-64.668
Hexadecane	7.914	2.568	0	-89.230	-89.075	-89.095
Nonadecane	9.414	3.030	0	-104.000	-103.818	-103.752
Octadecane	8.914	2.876	0	-99.080	-98.904	-98.866
Pentadecane	7.414	2.414	0	-84.310	-84.16	-84.210
Tetradecane	6.914	2.260	0	-79.380	-79.246	-79.324
Tridecane	6.414	2.106	0	-74.450	-74.331	-74.439

I = 0 for Straight Chain   I = 1 for Branched Chain

Table 7. Experimental and theoretical calculated values of ΔHf0 by E and R parameters in alkanes

Name of compound	E	R	ΔHf0		
			Exp.value	Cald.Eq.12	Cald.Eq.13
Methane	*	6.478	-17.890	*	-17.806
Ethane	4.000	11.125	-20.240	-20.611	-22.606
Propane	5.500	15.771	-24.820	-25.500	-27.405
n-Butane	7.000	20.418	-30.150	-30.389	-32.205
2-Methyl propane	7.333	20.418	-32.150	-31.475	-32.205
n-Pantane	8.500	25.065	-35.000	-35.279	-37.006
2-Methyl butane	8.833	25.065	-36.920	-36.364	-37.006
2,2-Dimethyl propane	9.250	25.065	-39.170	-37.723	-37.006
n-Hexane	10.000	29.712	-39.960	40.168	-41.806
2-Methyl pentane	10.333	29.712	-41.660	-41.253	-41.806
3-Methyl pentane	10.333	29.712	-41.020	-41.253	-41.806
2,2-Dimethyl butane	10.750	29.712	-44.350	-42.612	-41.806
2,3-Dimethyl butane	10.666	29.712	-42.490	-42.338	-41.806
Heptane	11.500	34.359	-44.880	-45.057	-46.606
2-Meyhyl hexane	11.833	34.359	-46.590	-46.142	-46.606
3-Mehtyl hexane	11.833	34.359	-45.960	-46.142	-46.606
2,2-Dimethyl pentane	12.250	34.359	-49.270	-47.501	-46.606
2,3-Dimethy pentane	12.166	34.359	-47.620	-47.228	-46.606
2,4-Dimethyl pentane	12.166	34.359	-48.280	-47.228	-46.606
2,2,3-Trimethyl butane	12.583	34.359	-48.950	-48.587	-46.606
Octane	13.000	39.005	-49.820	-49.946	-51.405
2-Methyl heptane	13.333	39.005	-51.500	-51.031	-51.405
3-Methyl heptane	13.333	39.005	-50.820	-51.031	-51.405
4-Methyl heptane	13.333	39.005	-50.690	-51.031	-51.405
2,2-Dimethyl hexane	13.750	39.005	-53.710	-52.391	-51.405
2,3-Dimethyl hexane	13.666	39.005	-51.130	-52.117	-51.405

2,4-Dimethylhexane	13.666	39.005	-52.440	-52.117	-51.405
2,5-Dimethylhexane	13.666	39.005	-53.210	-52.117	-51.405
3,3-Dimethylhexane	13.750	39.005	-52.610	-52.391	-51.405
3,4-Dimethylhexane	13.666	39.005	-50.910	-52.117	-51.405
Nonane	14.500	43.652	-54.740	-54.835	-56.206
2,2,3-Trimethylpentane	14.083	39.005	-52.610	-53.476	-51.405
2,2,4-Trimethylpentane	14.083	39.005	-53.570	-53.476	-51.405
2,3,3-Trimethylpentane	14.083	39.005	-51.730	-53.476	-51.405
2,3,4-Trimethylpentane	13.999	39.005	-51.970	-53.202	-51.405
3-Ethyl pentane	11.833	34.359	-45.330	-46.142	-46.606
3-Methyl-3-ethyl pentane	13.750	39.005	-51.380	-52.391	-51.405
					contd-
2-Methyl-3-ethyl pentane	13.666	39.005	-50.480	-52.117	-51.405
2,2,3,3-Tetramethylbutane	14.500	39.005	-53.990	-54.835	-51.405
Undecane	17.500	52.946	-64.600	-64.613	-65.806
Hexadecane	25.000	76.180	-89.230	-89.059	-89.806
Nonadecane	29.500	90.120	-104.000	-103.727	-104.206
Octadecane	28.000	85.473	-99.080	-98.838	-99.406
Pentadecane	23.500	71.533	-84.310	-84.170	-85.006
Tetradecane	22.000	66.886	-79.380	-79.281	-80.206
Tridecane	20.500	62.239	-74.450	-74.392	-75.406

III CONCLUSION:

Therefore, standard heat enthalpies of formation (ΔH_f^0) of alkanes can be estimated by equations(10),(11), (12) and (13) simply by calculating molecular connectivity ($^1\chi^v$) , van der waals volume (V_w), electrotopological state index (E) and refractotopological state index (R) parameters.

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