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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:** Samples of materials, collected at different stages of vermicomposting, were submitted to extraction procedures of humic acids. Titration, termogravimetry (DTG), X-ray diffraction, spectrophotometry in the uv/visible and infrared techniques, were used in the study of these materials. The data from the potentiometry titration analysis were submitted to adjustment by non-linear regression, determining thus five values of pKa's characteristic of five classes of titrable groups. In the DTG curves two stages can be observed, being the first one characteristic of the separation of aliphatic and/or alicyclic structures and the second of decomposition of aromatic structures. The X-ray diffraction technique exhibited marked differences in the results, mainly in the first three peaks, were a structural reorganization and a polymerization along the vermicomposting process. The infrared spectra practically no differentiation between the samples. The values for the ratio  $E_4/E_6$  found are in accordance with the characteristic values for humic acids, but do not supply information that can contribute to the elucidation of the structure and formation of these acids.

**Keywords:** titration, termogravimetry, diffraction, spectrophotometry, non-linear regression.

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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<sup>7,8</sup>. The aim of this paper is to obtain the correlation equations of ( $\Delta H_f^0$ ) with  $^1X^v$ , Vw, E and R parameters.

### 1. Calculation of Kier's<sup>9</sup> molecular connectivity ( $^1X^v$ ):

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

**Table 1.** Atom connectivity ( $\delta i^v$ ) values in different groups

Groups	$\delta i^v$	Groups	$\delta i^v$
- CH <sub>3</sub>	01	= CH <sub>2</sub>	02
≡ CH	03	- OH	05
-NH <sub>2</sub>	03	O	06
-NH -	04	C = O	06
- C ≡ N	05	Furan O	06
- C = NH	04	O = N O	06
N or Pyridine N	05	H <sub>2</sub> O	04
NH <sub>3</sub>	02	F	(-) 20
NH <sub>4</sub>	01	Cl	0.690
> N < +	06	Br	0.254
= N H <sub>2</sub> +	03	I	0.085

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

Here the sum is the overall connections or edges in such a graph,  $\delta i^v$  and  $\delta j^v$  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 ( $\delta i^v$ ) is defined as

$$\delta i^v = \frac{Z_i^v - h_i}{Z - Z_i^v - 1} \quad (2)$$

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

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

### 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  $I_i$  plus a perturbation given by the electronic influence of the topological environment of the molecule<sup>13-15</sup>. Intrinsic state valence  $I_i$  of each atom is calculated as follow:

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

Where  $N$  is the principal quantum number of the atom  $i$ ,  $\delta v$  the number of valence electrons in the skeleton ( $Z_v - h_i$ );  $\delta$  the number of  $\sigma$  electrons in the skeleton ( $\sigma - h$ ). For a skeleton,  $Z_v$  the total number of electrons on the atom,  $\sigma$  the number of electrons in the  $\sigma$  orbitals,  $h$  the number of

bonded hydrogen atom. E-state for an atom  $i$  in molecule ( $S_i$ ) is given by

$$S_i = I_i + \sum \Delta I_i \quad (5)$$

$\Delta I_i$  quantifies the perturbation effect on the intrinsic atom value. This perturbation is assumed to be a function of the difference in the intrinsic values  $I_i$  and  $I_j$ :

$$\Delta I_i = \sum (I_i - I_j) / r_{ij}^2 \quad (6)$$

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  $\Delta I_i$  for a pair of skeletal atoms encode both electronic and topological attributes that arise from electronegativity differences and skeletal connectivity. Therefore, the total of sum of the differences in intrinsic values,

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

$$S_i = I_i \quad (7)$$

Therefore, E-state for a molecule =  $\sum n_i S_i$  or  $\sum n_i I_i$  (8)

**Table 4.** Intrinsic state valence  $I_i$  of atoms in some groups

Group	$I_i$	Group	$I_i$	Group	$I_i$
$>C<$	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<sup>16</sup> 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<sup>16</sup>) is based on the idea that the sum of the atomic values ( $\alpha_i$ )

being related to the molecular value of the molar refractivity:

$$R(\text{molecule})_{\text{calc.}} = \sum n_i \alpha_i \quad (9)$$

Where,  $n_i$  = No. of atoms;  $\alpha_i$  = Atomic refractivity value

**Table 6.** Experimental and theoretical calculated values of  $\Delta H_f^0$  by 1Xv & Vw parameters in alkanes

Name of compound	1Xv	Vw	I	$\Delta H_f^0$		
				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-Pentane	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-Methyl hexane	3.269	1.132	1	-46.590	-48.290	-48.519
3-Methyl 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-Dimethyl 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

contd-

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 ( $\Delta H_f^0$ ) 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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