ANALELE UNIVERSITATII BUCURESTI
Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

HANDRICK METHOD APPLIED TO ISOBUTYL PHENYL ACETONITRILE DERIVATIVES

Viorica Meltzer*, Elena Pincu and Gabriela Cristescu

abstract Heat of combustion for a series of isobutyl phenyl acetonitrile derivatives are calculated using Handrick method. The literature experimental results were compared with theoretical data obtained from Handrick group contribution method. For all six isobutyl phenyl acetonitrile derivatives, calculated and measured heat of combustion differ only ± 0,14 % on average

Introduction

The heat of combustion can be calculated from empirical equations and group contribution methods [1,2]. Often, the empirical equations are in conflict with experimental data. The group contribution takes into account the compound structures and gives good results with experimental data [3]. One of these group contribution methods is Handrick method, which is property for complex structures of organic compounds with different aggregation states.

In this paper heat of combustion for a series of isobutyl phenyl acetonitrile derivatives are calculated using Handrick method.

The heat of combustion was definited for the relation:

$$C_aH_bN_cO_dX_eS_f + \left[\frac{2(a+f)-d+\frac{(b-e)}{2}}{2}\right]O_2 \rightarrow$$
$$\rightarrow aCO_2(g)+\frac{b-e}{2}H_2O(l)+\frac{c}{2}N_2(g)+e\,HX(l)+f\,SO_2(g) \qquad (1)$$

The number of oxygen atoms required:

$$x = 2(a+f)-q+\frac{(b-e)}{2} \qquad (2)$$

is called the molar oxygen balance. The basic tenet of the method is that the heat of combustion is a linear function of x, that is:

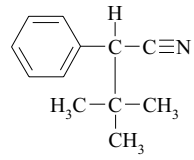
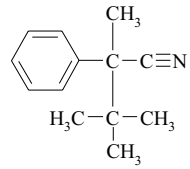
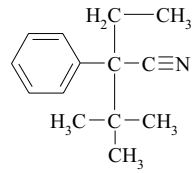
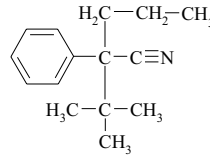
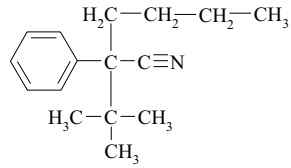
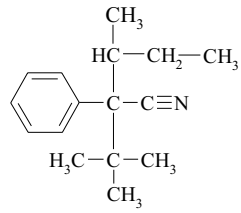
* University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, Bd. Regina Elisabeta 4-12, Bucharest, Romania, 030018, e-mail: viomel@gw-chimie.math.unibuc.ro

$$-\Delta_c H^o_{298} = \sum a' + x \sum b' \quad (3)$$

where a' and b' are tabulated for a large number of structural groups.

Results and discussion

Table 1 **The structure of isobutyl phenyl acetonitrile derivatives**

no.	Name	Structure	Molecular weight
1	Isobutyl phenyl acetonitrile		173,26
2	Methyl isobutyl phenyl acetonitrile		187,29
3	Ethyl isobutyl phenyl acetonitrile		201,31
4	n-propyl isobutyl phenyl acetonitrile		215,34
5	n-butyl isobutyl phenyl acetonitrile		229,37
6	sec-butyl isobutyl phenyl acetonitrile		229,37

A lot of experimental results allowed choosing the models of calculus for different organic compounds.

The structures and molecular weight of isobutyl phenyl acetonitrile derivatives are presented in Table 1.

Experimental data [4] was compared with theoretical data obtained from group contribution by Handrick method, which is much more appropriate for the structure of studied compounds.

For all six compounds, the following groups contributed to establish the heat of combustion:

- n-paraffin;
- branched paraffin;
- benzene;
- nitrile.

for which a' and b' involved in equation (3) are given in Table 2.

Table 2 Coefficient of equations for heat of combustion

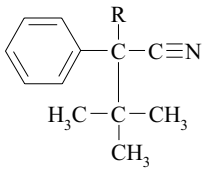
Functional group	a'	b'
n-paraffin	+ 5,7	+ 52,08
branched paraffin	- 3,7	+ 0,09
benzene	- 10,1	+ 0,07
nitrile	+ 9,3	- 0,01

Calculated and also experimental values for heat of combustion are shown in Table 3.

Table 3 Calculated and experimental values for heat of combustion

Compound	x (rel. 2)	$\Delta_c H^0$ (kcal · mol^{-1})		$\Delta_c H^0_{exp} - \Delta_c H^0_{th}$	Relative error %
		Experimental [4]	Theoretical		
1	$\frac{63}{2}$	1647,02	1646,45	0,57	0,035
2	$\frac{69}{2}$	1804,80	1803,14	1,66	0,092
3	$\frac{75}{2}$	1962,20	1959,83	2,37	0,121
4	$\frac{81}{2}$	2119,62	2116,52	3,10	0,146
5	$\frac{87}{2}$	2277,02	2273,21	3,81	0,168
6	$\frac{87}{2}$	2279,30	2273,21	6,09	0,268

General structure of isobutyl phenyl acetonitrile derivatives is presented bellow:



were R = H, CH_3, C_2H_5, C_3H_7, n-C_4H_9, sec- C_4H_9.

Dependence $\Delta_c H = \Delta_c H\left(n_{CH_2}\right)$, with n_{CH_2} the number of CH_2 group from R, for experimental and theoretical values are shown in Fig. 1.

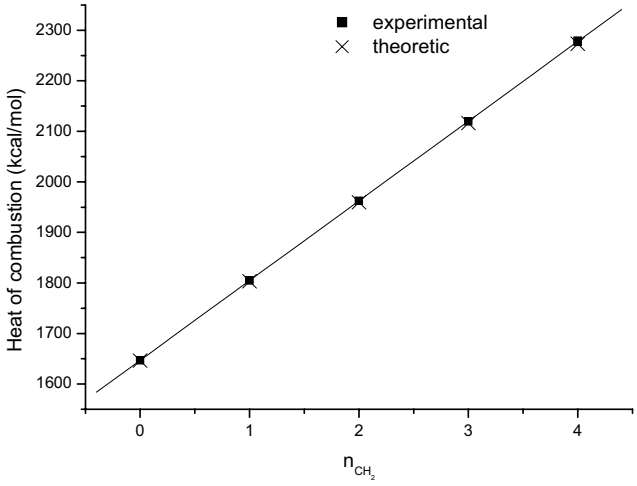


Fig. 1 $\Delta_C H^0 = \Delta_C H^0\left(n_{CH_2}\right)$

In both cases it is obviously a linear dependence described by the following equations:

- experimental $\Delta_C H^0 = 1646.89 + 157.75 \cdot n_{CH_2}$ (4)
- theoretical $\Delta_C H^0 = 1646.45 + 156.69 \cdot n_{CH_2}$ (5)

Conclusions

The theoretical data should correlate well with measured heat of combustion. In fact, calculated and measured heat of combustion differ by only ± 0.14 % on average.

Relative error increase with increase of number of – CH_2 – groups from R radical.

Handrick method not allowed differentiation between heat of combustion values of normal and secondary R.

For isobutyl phenyl acetonitrile derivatives heat of combustion can be calculated with equation (4) or (5). The differences between experimental and theoretical values of heat of combustion are in the range of error admissible in thermochemistry.

REFERENCE

1. Benson, S.W., Cruickshank, F.R. and Golden, D.M. (1969) *Chem. Rev.* **69**(3), 279.
2. Reid, R.C. and Sherwood, J.M. (1966) **The properties of gases and liquids**, Mc Grow Hill, New York, 221-30.
3. Meltzer, V., Pincu, E. and Cristescu, G. (2007) *Anal. Univ. Buc. Chimie*, anul **XVI** (serie noua), vol. **I**, 21-4.
4. Zavoianu, D. and Ciocazanu, I. (2000) *Rev. Chim.* (Bucuresti) **51**(8), 607-9.