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ALKYL INDUCTIVE EFFECTS ON MOLECULAR IONIZATION POTENTIALS—XV

n-ALKANES

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Abstract—The first ionisation potentials, E_I, of n-alkanes are found to be a linear function of the inductive substituent constants, $\Sigma\sigma_I$. The correlation is obtained by considering that a σ-bonding electron is ejected from the most central C—C bond in the alkane R—R'. The equation for the regression is $E_I = 17{\cdot}19 + 60{\cdot}2\,\Sigma\sigma_I \pm 0{\cdot}04$ eV, with correlation coefficient 0·998. An equation is also deduced relating E_I to the number of carbon atoms, n_c, and hydrogen atoms, n_H, in the n-alkane: $E_I = 4{\cdot}70(n_H - 1)/n_c$, from which E_I for polymethylene, $(CH_2)_x$, is found to be 9·40 eV.

In this paper it will be demonstrated that the adiabatic ionization energies, E_I, of n-alkanes are linear functions of Taft's inductive substituent constants, σ_I.[1]

It has already been shown that the ionization potentials of alkyl free radicals,[2] R·, are linear in σ^*,[3] and that the E_I's of alcohols,[4a] ethers,[4b] thiols,[4c] thioethers,[4d] alkyl halides,[4e] ketones,[4f] carboxylic acids,[4g] copper acetylacetonates,[4h] amines,[4i] esters,[5] nitriles,[6] nitroalkanes,[6] disulfides,[7] alkenes,[8] and alkynes,[9] are all linear with respect to both σ_I and σ^*. Thus one is able to compute, with a high degree of precision, the ionization potentials of compounds which yield a low abundance of the primary cation radical, or are difficult to obtain in a pure state, or vaporize only with decomposition.

The first adiabatic ionization energy of alkanes corresponds to the ejection of an electron from the highest occupied MO,[10] which is assumed, with the exception of methane, to be a σ bonding orbital mainly associated with C—C, rather than C—H, the C—C bond being weaker than the C—H bond (82 and 100 kcal/mol, respectively). In order to compute the proper $\Sigma\sigma_I$, we assume that the ejected electron is from that C—C bond which has the highest electron density, due to interelectron repulsion. Electron release by alkyl groups is in accordance with their usual inductive order (Me < Et < n-Pr, etc.) and is, of course, reflected in the σ_I and σ^* constants. For a n-alkane this is tantamount to saying that the electron is lost from the most central C—C bond in the molecule. For n-butane, for example, $\Sigma\sigma_I$ will be calculated for two ethyls, *not* a methyl and n-propyl. Only in this way is the correlation obtained.

We can write, therefore, the following representation of the gas-phase expulsion of a σ-bonding electron from a C—C bond:

$$R{\odot}R' \xrightarrow{E_I} R\overset{+}{\odot}R' + e^-$$

where R and R' cannot differ by more than one carbon (when n is odd in C_nH_{2n+2}).

Unlike the correlations given in previous papers in this series,[4-9] we are not able to include the simplest of the n-alkanes, methane, due to the absence of a C—C bond; and in this respect it is not surprising that the E_I value for CH_4 (13 eV) falls far from the regression line. Furthermore, in this series of compounds, there is no functional group in the accepted sense.

Table 1 lists the available experimentally[11] obtained photoionization (PI) potentials for the n-alkanes, along with the corresponding $\Sigma\sigma_I$ values for the alkyl groups, computed as explained above.

The experimental E_I values are plotted *vs* $\Sigma\sigma_I$ in

Table 1. Experimental and calculated E_I values

Cmpd	$\Sigma\sigma_I{}^a$	E_I (eV) (Expt'l)^b	Calculated E_I (eV) (Eq (2))	(Eq (5))	(Eq (7))
C_2H_6	−0·092	11·65	11·65	11·78	11·75
C_3H_8	−0·101	11·07	11·10	10·98	10·97
C_4H_{10}	−0·110	10·63	10·56	10·59	10·58
C_5H_{12}	−0·113	10·35	10·38	10·35	10·34
C_6H_{14}	−0·116	10·18	10·20	10·19	10·18
C_7H_{16}	−0·118^c	10·08	10·08	10·08	10·07
C_8H_{18}	−0·120^c	—^{d}	9·95	9·99	9·98
C_9H_{20}	—^{e}	—^{d}	—	9·93	9·92
$C_{10}H_{22}$	—^{e}	—^{d}	—	9·88	9·87
$(CH_2)_x$	—	—^{d}	—	9·40	9·40

[a] From Ref 1.
[b] From Ref 11.
[c] n-Bu value from Ref 4*a*.
[d] Experimental PI or PES value not available.
[e] The σ_I for n-Am is not known.

Fig 1, where it is immediately evident that an excellent correlation exists (r = 0·998; standard error = 0·04 eV).

The equation for the regression line is given by

$$E_{R-R} = E_0 + a_I \Sigma \sigma_I. \quad (1)$$

The intercept (E_0) and slope (a_I) are found to be 17·19 eV and 60·2 eV, respectively, and therefore we have:

$$E_{R-R} = 17 \cdot 19 + 60 \cdot 2\, \Sigma \sigma_I \pm 0 \cdot 04\ \mathrm{eV}. \quad (2)$$

In the fourth column of the Table, the E_I values calculated using Eq (2), are presented, and the agreement with the experimental values is seen to be excellent. The E_I's are also computed for n-octane, n-nonane, and n-decane, compounds for which there are as yet no experimental PI, PES, or spectroscopic values available.

The slope, a_I, in eV units, is analogous to the dimensionless reaction constant ρ_I, and is a measure of the sensitivity of the ionization site to alkyl inductive effects. The very large a_I value of 60·2 obtained here for n-alkanes should be compared with the slopes observed for alkyl free radicals[3] (15·2)*, alkenes[8] (11·6), alkynes[9] (23·2), ethers[4h] (28·0), and ketones[4f] (14·0). For alkenes and alkynes a bonding π-electron is lost. Comparing the n-alkanes with the ethers and ketones, it is seen that the a_I's vary tremendously in the order $R_2CO \ll R_2O \ll R{-}R$, and this can be rationalized in the following way: in R_2CO the ionization site is the oxygen lone pair and the alkyl inductive effect must be transmitted through the carbonyl carbon and the C=O double bond; in R_2O the electron is lost again from an oxygen non-bonding lone pair, but the R groups are in close proximity; In R : R the alkyl groups are at the very site of ionization and thus are able to exert the strongest inductive effect.

It is seen from the experimental E_I data in the Table that there is a regular but gradual attenuation of the diminishing effect of increased chain length on the ionization potentials. This is shown more clearly in Fig 2 where E_I is plotted against the number of C atoms, n. This curve is, apparently, a rectangular hyperbola, and can be represented[12] by Eq (3):

$$E_I = E_{(min)} \left(\frac{n+b}{n} \right), \quad (3)$$

where $E_{(min)}$ is the theoretical E_I value for a straight chain saturated hydrocarbon of infinite length, i.e., for polymethylene; and *b* is an empirical constant to be evaluated. In order to determine the numerical values of $E_{(min)}$ and *b*, Eq (3) can be rearranged to give Eq (4)

$$nE_I = nE_{(min)} + bE_{(min)} \quad (4)$$

which is the equation for a straight line (Fig 3) in a plot of nE_I *vs* n, with intercept $bE_{(min)}$ and slope $E_{(min)}$. The slope is found to be 9·40 eV and the intercept is 4·75 eV, from which b = int./slope =

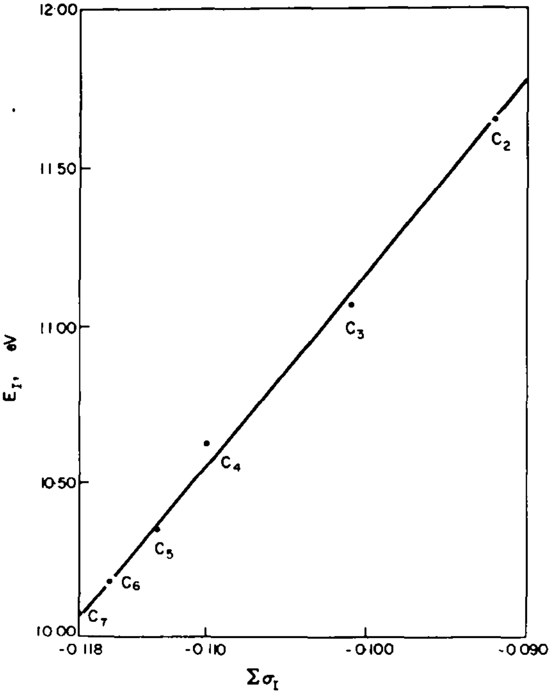

Fig 1.

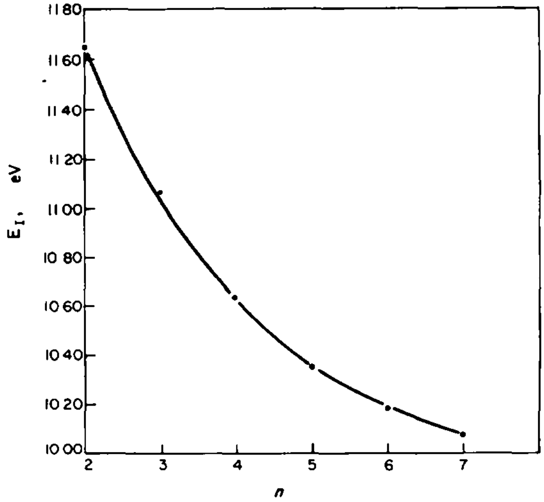

Fig 2. A plot of E_I of C_nH_{2n+2} vs n.

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*Value obtained by our plot of E_I against σ_I (unpublished work).

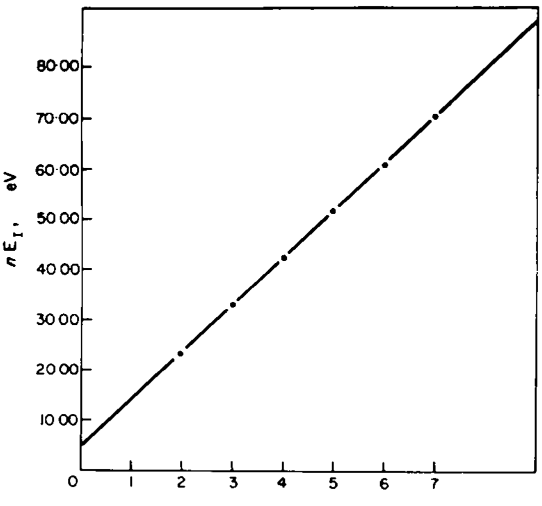

Fig 3. A plot of nE_I of C_nH_{2n+2} vs n.

0·505. Substituting these values into Eq (4), we have

$$nE_I = 4{\cdot}75 + 9{\cdot}40\,n \pm 0{\cdot}05\ \text{eV}. \tag{5}$$

With good approximation, $b = \frac{1}{2}$, and therefore Eq (3) can be rewritten as

$$E_I = 9{\cdot}40\left(\frac{n+\frac{1}{2}}{n}\right), \tag{6}$$

which can be rearranged to give

$$E_I = 4{\cdot}70\left(\frac{2n+1}{n}\right) = 4{\cdot}70\left(\frac{n_H - 1}{n_C}\right)$$
$$= 4{\cdot}70(2) \text{ for } 2n \gg 1, \tag{7}$$

where n and n_C = number of C atoms and n_H the number of H atoms in the alkane C_nH_{2n+2} ($n \neq 1$). This single parameter equation can be compared to the three parameter equation* of Vilesov[13] who has estimated $E_{I(min)}$ (for $(CH_2)_x$) to be 9·06 eV, whereas Herndon,[14] Hall,[15] and Fukui, *et al.*,[16] using various semi-empirical MO methods, have all estimated $E_{I(min)}$ at about 10·0.†

$${}^*E_I = 9{\cdot}06 + \frac{A}{n_C} - \frac{B}{n_C^2}.$$

†Calculations based on vertical electron impact E_I's which generally run 0·5 to 1·0 eV higher than those obtained by PI, PES, or spectroscopy.

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