

# STERIC EFFECT I—CHARTON'S PARAMETER vs TOPOLOGICAL INDEX

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## ABSTRACT

Topology of branching at  $\alpha$  position in the first order hydrolysis of ethyl or methyl ester is discussed. Charton's parameter for steric effect is correlated with topological index of the non-reacting part of the molecule which, therefore, provides a new steric parameter.

## INTRODUCTION

**M**OLECULAR topology is a new discipline of theoretical chemistry which finds its applications in organic chemistry<sup>1</sup>. New topological indices are introduced by several workers<sup>2-5</sup> and correlation of these indices with the physical and chemical properties of the similar systems is obtained. The method was recently applied to a number of linear<sup>1</sup> and cyclic systems<sup>6</sup>.

Many organic reactions at the functional group are influenced by the rest of the molecule<sup>7</sup>. This can either stop or increase or alter the course of the reaction. The effect of structure on chemical reactivity can be divided into field effects, resonance or mesomeric effects and steric effects.

The steric effect was first treated quantitatively by Taft<sup>8</sup> who proposed a parameter  $E_s$  characteristic of the non-reacting part of the system. It was found later<sup>9</sup> that the Taft's parameter  $E_s$  was linear in van der Waal's radii of the groups and therefore it measures the true steric effect. The parameter  $E_s$  was defined as

$$E_s = \log(k/k_0), \quad (1)$$

where  $k$  and  $k_0$  are the rate constants for acid catalyzed hydrolysis of the substituted ester and the ester bearing a methyl group in the acyl part. Charton introduced a new steric parameter<sup>9,10</sup>  $\nu$  which was based on van der Waal's radii of the non-reacting part. This is defined as

$$\nu_x = r_{vx} - r_{vH}, \quad (2)$$

where  $r_{vx}$  is the van der Waal's radius of the group  $X$ , and  $r_{vH}$  is the van der Waal's radius of the hydrogen atom.

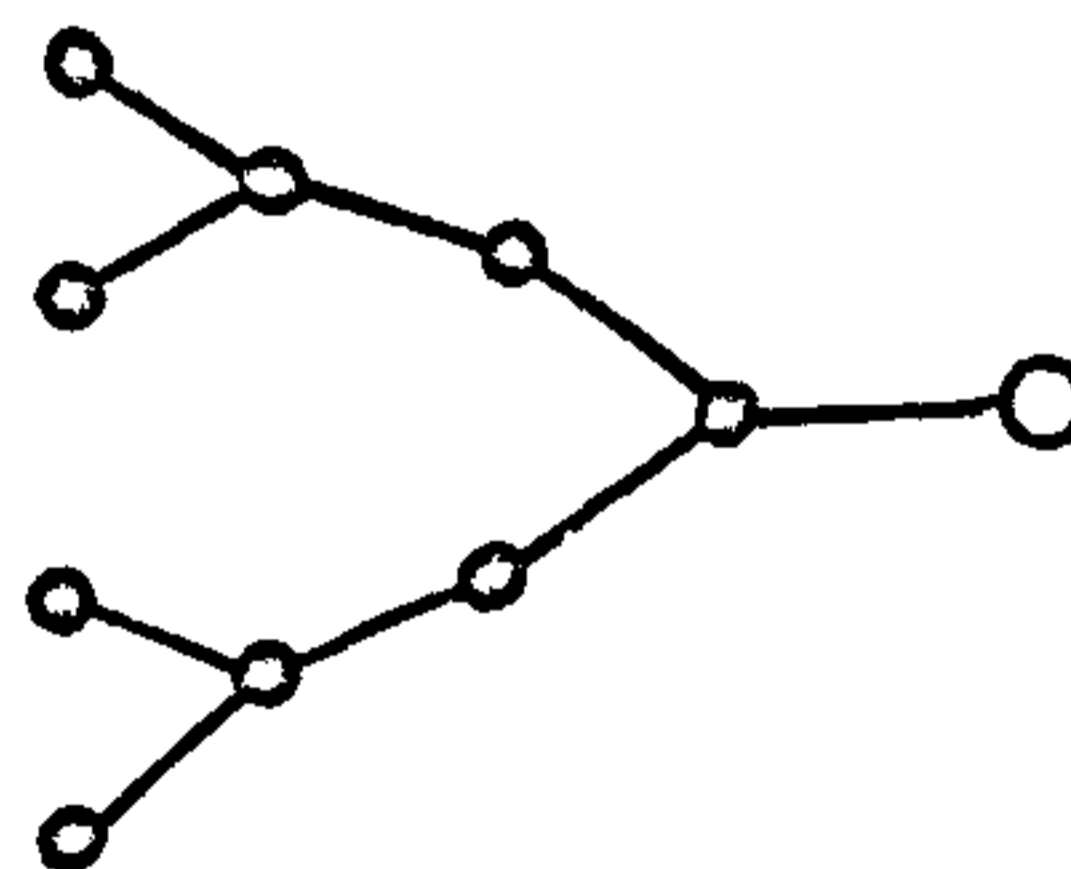
Recently studies on steric effect were made by Motoc<sup>11</sup> who applied graph theory to calculate the steric difference<sup>11-13</sup> by defining a new steric parameter. Balaban<sup>14</sup> used topological indices to fit the steric parameter. In the present work we show that Charton's parameter<sup>15</sup> which was based on the van der Waal's radii, can be correlated with topological branching index<sup>16</sup> and therefore the branching index may be used as a quantitative measure of the steric effect.

## METHOD

Graph theory<sup>17</sup> can be applied to construct the component graphs of the non-reacting part of the molecules. The molecular graphs of the system are considered with a vertex of different colour symbolizing the functional group or the reaction site. The component graph of the non-reacting part of the molecule is considered as a basis and the branching index is calculated using the relation,

$$\chi = \sum_{ij} \frac{1}{(d_i d_j)^{1/2}}, \quad (3)$$

where  $d_i$  and  $d_j$  are the degrees of the adjacent vertices  $i$  and  $j$  and the summation is taken over all pairs of the adjacent vertices. The tree growing<sup>17</sup> and  $\alpha$  position of the group is shown in figure 1.



The closed circle represents the carbon atom and the open circle represents the reaction site. The whole graph thus represents a non-reacting group (i-PrCH<sub>2</sub>)<sub>2</sub>CH in the whole molecule. Thus by using simple topological branching index<sup>16</sup> a measure of topological volume for non-reacting part of the molecule could be defined. Considering the first order hydrolysis of the esters XCOOC<sub>2</sub>H<sub>5</sub> or XCOOCH<sub>3</sub> and branching at  $\alpha$  position by constructing graphs of the groups  $X$ , we have correlated the branching index with the Charton's parameter  $\nu$ . The correlation is shown under different classes of trees, linear groups and trees with rings. The phenyl group is taken as ring.

TABLE 1

Values of parameter  $\nu$  and branching index  $\chi$  for linear chains

Group X	$\nu^a$	$\chi$
Me	0.52	1.000
Et	0.56	1.414
Pr	0.68	1.914
Bu	0.68	2.414
BuCH <sub>2</sub>	0.68	2.914
BuCH <sub>2</sub> CH <sub>2</sub>	0.73	3.414
BuCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	0.73	3.914
BuCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	0.68	4.414

<sup>a</sup>Ref. 10, Table 3, Me = Methyl, Et = Ethyl, Pr = Propyl and Bu = Butyl.

TABLE 2

Parameter  $\nu$  and index  $\chi$  for trees at  $\alpha$  position

Group X	$\nu^a$	$\chi$
<i>i</i> -Pr	0.76	1.732
<i>i</i> -PrCH <sub>2</sub>	0.98	2.270
<i>t</i> -Bu	1.24	2.000
<i>t</i> -BuCH <sub>2</sub>	1.34	2.561
Et <sub>2</sub> CH	1.51	2.808
Pr <sub>2</sub> CH	1.54	3.808
Bu <sub>2</sub> CH	1.56	4.808
( <i>i</i> -PrCH <sub>2</sub> ) <sub>2</sub> CH	1.70	4.417
( <i>t</i> -BuCH <sub>2</sub> ) <sub>2</sub> CH	2.03	5.100
<i>t</i> -BuCH <sub>2</sub> CHMe	1.41	3.416

<sup>a</sup>Ref. 10, Table 3.

TABLE 3

Parameter  $\nu$  and index  $\chi$  for groups with rings

Group X	$\nu^a$	$\chi$
Ph	0.57	3.393
PhCH <sub>2</sub>	0.70	3.931
PhCH <sub>2</sub> CH <sub>2</sub>	0.70	4.431
PhMeCH	0.99	4.303
PhEtCH	1.18	4.841
Ph <sub>2</sub> CH	1.25	6.876

<sup>a</sup>Ref. 10, Table 3, Ph = Phenyl.

## DISCUSSION

With the increasing size of the non-reacting part X of the ester XCOOR, where R represents the methyl or ethyl group, the rate of hydrolysis changes according to Charton's relationship<sup>10</sup>,

$$\log k = \Psi \nu + h, \quad (4)$$

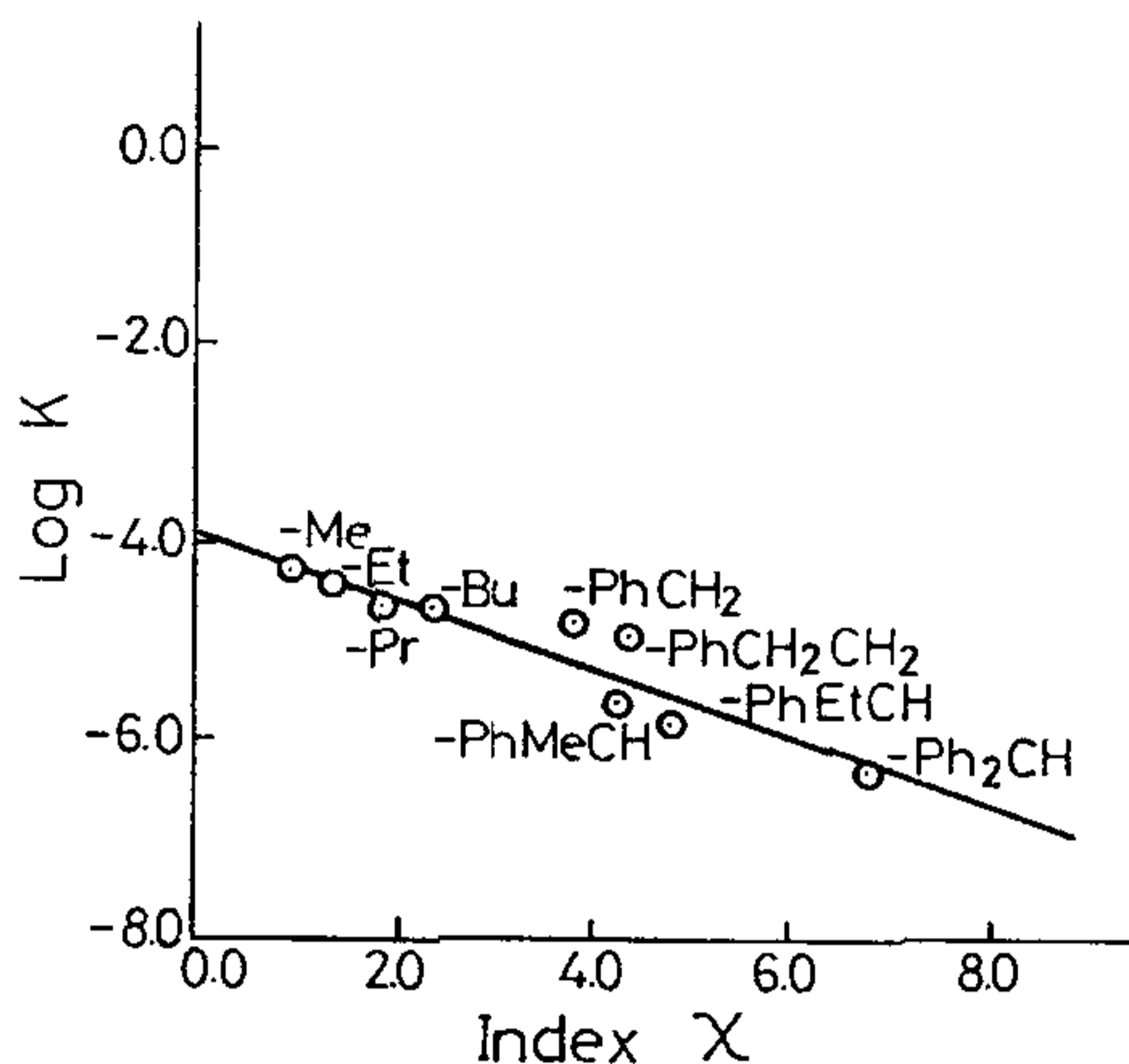
where  $\Psi$  and  $h$  are constants for different sets of reactions. The parameter  $\nu$  depends upon the van der Waal's radii of group X. The topological index such as the branching index depends upon the arrangement of different vertices (atoms) in different positions in space and hence the topological branching index may define a measure of the volume of the non-reacting part X. The branching index values may therefore be used in quantitative treatment of steric effect. Table 1 shows the effect of linear chains on parameter  $\nu$ . Tables 2 and 3 correlate the Charton's parameter  $\nu$  with topological indices of trees at  $\alpha$  position and trees with rings respectively. For linear chains at  $\alpha$  position, the topological index increases while the parameter  $\nu$  has very little effect. These correlations show that the topological index varies with the size of the molecule or a portion of the molecule as is clear from tables 2 and 3. The effect of molecular size on chemical reactivity could thus be expected. For the groups with rings (phenyl) the parameter  $\nu$  increases in proportion to the index  $\chi$ . The correlation coefficients calculated for steric effect of trees at  $\alpha$  position and trees with rings (tables 2 and 3) are 0.4250 and 0.1875 respectively. The standard deviation for the reported data from correlation is 0.1887 approximately. We have considered a number of reactions, the different sets of acid catalyzed hydrolysis of esters at different temperatures<sup>18-20</sup>. The rate constants were correlated with the topological indices of the non-reacting part of the esters. At constant temperature  $\log k$  was found to be a linear function of index  $\chi$ .

$$\log k = a\chi + b, \quad (5)$$

where  $a$  and  $b$  are constants depending upon the experimental conditions. The slope  $a$  of the correlation equation varies regularly with temperature. Figure 2 shows the dependence of  $\log k$  on index  $\chi$ ; for the reaction rate data<sup>19</sup> of a set of acid catalyzed hydrolysis of ethyl esters in 70% methylacetate—water (v/v) at 25°. The intercepts and the slope of the straight line are,

$$b = -3.85 \text{ and } a = -0.350$$

For a narrow temperature range, the activation energy  $E_a$  can be calculated by using the well-known relationship,



**Figure 2.** A plot of  $\log k$  vs index  $\chi$  for acid catalyzed hydrolysis of ethyl esters at  $25^\circ$  (data from ref. 19 & 20).

$$\log \frac{k_2}{k_1} = \frac{E_a}{R} \frac{(T_2 - T_1)}{T_1 T_2} \quad (6)$$

The enthalpy of activation  $\Delta H^\ddagger$  can also be calculated using the approximation<sup>21</sup>,

$$E_a \simeq \Delta H^\ddagger + RT \quad (7)$$

For a number of reactions at different temperatures  $\Delta H^\ddagger$  generally depends linearly upon the index  $\chi$ <sup>22</sup>. This agrees with the linear free energy relationship<sup>23</sup>.

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