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STERIC EFFECTS OF ALKYL GROUPS: A 'CONE ANGLE' APPROACH

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A 'cone angle', θ_R, is defined for an alkyl group (R), which is proposed as a measure of the steric effect exerted by the group. The θ_R values for some 57 groups have been calculated mathematically by constructing the corresponding Corey–Pauling–Koltun molecular models. The variation in θ_R with the bulk of a group is satisfactory. However not all types of alkyl groups can be accommodated in this cone angle approach. In the case of the groups for which the cone angle can be measured, correspondences between θ_R and the two existing steric parameters (Taft's E_s scale and Dubois' E_s' scale) have been established. For some 23 alkyl groups θ_R has been used to explain the variation in the rate constant of the base-catalysed hydrolysis of RCOOEt with the nature of R. Our studies independently substantiate the basic assumptions of the Taft–Ingold hypothesis that, while the base-catalysed ester hydrolysis is mostly controlled by the steric and electronic effects of the R group, the acid-catalysed one is controlled almost solely be the steric effect.

INTRODUCTION

Since 1895 several efforts[1–4] have been made to quantify the steric effect of an alkyl group. However, it was only in the 1950s that Taft[5] first formulated a steric parameter E_s for this purpose. To develop the E_s scale he used the hypothesis, following a suggestion of Ingold,[6] that other factors being the same, acid-catalysed hydrolysis of esters is controlled by steric effects only. The E_s was defined by equation (1) with respect to a

$$E_s = \log(k/k_0)_{\text{acid}} \tag{1}$$

reference substituent Me (the subscript 0 refers to Me) using the average rate data for four closely related reactions involving acid-catalysed ester hydrolysis and esterification of carboxylic acids. Although the success of Taft's scale over the decades is well known, this scale has been criticised by several workers on various occasions.[4,7–10] Dubois has argued that Taft's E_s scale lacks a single reference reaction; by designing a single reference reaction and using equation (1) he has formulated[10] another scale, E_s', for a large number of alkyl groups. In general, for most of the alkyl groups the E_s' values are close to the E_s values. Later Dubois found[11] a very good correspondence between the topological features of an alkyl group and its E_s' value. Because of the inherent assumptions of the Taft–Ingold hypothesis several authors felt that the E_s contains some amount of electronic effect and attempted modifications of the numerical values.[4,7] The limitations of the hypothesis have been discussed by Shorter.[12] In this paper we shall develop a new steric parameter for an alkyl group in an attempt to generate a steric scale not vitiated by the electronic effects of the group. We shall then compare our parameter with the existing scales to examine various aspects of the Taft–Ingold hypothesis.

AN APPROACH

In order to formulate a steric parameter free from electronic effects, the best approach is to consider the physical properties of a group rather than the chemical ones. The most reasonable physical property that can be related with the steric effect is the size of a group. This was realised long ago. In 1895 Wegscheider[2] first indicated that the 'steric hindrance' of a substituent can be related to its volume. Much later, for a few symmetrical alkyl groups, the calculated volumes have been shown to be a measure of the steric effect.[13,14] The Van der Waals' radius of a group or some modifications

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Table 1. Cone angle data, some measures of steric effect and other data for various alkyl and other groups used in the present study[a]

No.	Group	θ_R	$-E_s$	$-E_s'$	$\log(k/k_0)_{base}$	χ^H
1	H	84[b]	-1·24	-1·12	2·45	2·21
2	F	90[b]	-0·78		8·42	3·90
3	I	91[b]	0·16		5·74	2·52
4	Br	91[b]	-0·08		7·02	2·62
5	Cl	92[b]	-0·27		7·56	2·95
6	CN	95[b]	-0·73		8·87	3·84
7	Me	112	0·00	0·00	0·00	2·27
8	CH_2F	119	0·24	0·20	2·49	2·61
9	CH_2Me	123	0·07	0·08	0·32	2·28
10	CH_2CN	124	0·94	0·89	2·28	2·96
11	$CH_2NH_3^+$	124	2·30			
12	CHF_2	127	0·67	0·32	4·41	3·00
13	CH_2Cl	128	0·24	0·18	2·36	2·64
14	CH_2Br	130	0·27	0·24	2·21	2·64
15	CH_2I	133	0·37	0·30	1·74	2·59
16	$CHMe_2$	135	0·47	0·48	-0·94	2·28
17	CF_3	135	1·16	0·78	5·16	3·46
18	CHMeCl	139	0·50			
19	CH_2CH_2Cl	139	0·90		0·05	2·49
20	CHMeBr	141	0·93			
21	$CH_2CH_2NH_3^+$	142	1·82			
22	CH_2CH_2Br	142	1·27			
23	CH_2Et	143	0·36	0·31	-0·68	2·28
24	CH_2(*n*-Pr)	143	0·39	0·31	-0·71	2·29
25	$CH(CH_2)_2Cl$	143	0·48			
26	$CH_2(CH_2)_2F$	143	0·40			
27	$CH_2(CH_2)_3CH_3$	143	0·40	0·31		
28	$CH_2(CH_2)_4CH_3$	143	0·44			
29	$CH_2(CH_2)_6CH_3$	143	0·53			
30	$CH_2(CH_2)_2Ph$	143	0·45	0·34	-0·40	2·40
31	$CH_2(CH_2)_3Ph$	143		0·33		
32	$CHCl_2$	144	1·54	0·58	3·27	2·99
33	CHMeI	144	1·36			
34	CH_2CH_2I	145	1·02			
35	CH_2CH_2CN	146	0·90			
36	CMe_3	146	1·54	1·43	-2·28	2·29
37	$C(CN)Me_2$	147	0·76			
38	$CHBr_2$	148	1·86	0·76		
39	CMe_2Br	153		1·77		
40	CHI_2	154		0·93		
41	CHMeEt	154	1·13	1·00		
42	CHMe(*n*-Pr)	154		1·02		
43	CHMe(*n*-Bu)	154		1·06		
44	CCl_3	160	2·06	1·75	4·51	3·30
45	$CMeBr_2$	160		1·92		
46	CBr_3	167	2·43	2·24		
47	$CHEt_2$	174	1·98	2·00	-2·54	2·29
48	CHEt(*n*-Pr)	174		2·00		
49	CHEt(*n*-Bu)	174		2·03		
50	CH(*n*-Pr)$_2$	174	2·11	2·03		
51	CH(*n*-Bu)$_2$	174		2·08		
52	CI_3	175		2·62		
53	$CMeEt_2$	186		3·63		
54	$CMePh_2$	201	3·55	3·73		
55	CEt_3	205	3·80	5·29		
56	$CEtPh_2$	221	4·34	4·55		
57	CPh_3	228	4·68	4·91		

[a] Meanings of the symbols used are same as in the text. The θ_R values are given in degrees. The E_s data are taken from Ref. 4 and the E_s' data from Ref. 10. $\log(k/k_0)_{base}$ value for an R group was calculated via equation (7) using the corresponding σ^* (from Ref. 5) and E_s parameters. The χ^H values, given in Pauling's units, are taken from Ref. 26.

[b] Calculated by equation (4).

have been used as steric parameters.[8,15] The main difficulty with the approaches involving the calculation of the volume of a group is that these fail to enumerate the effects of the conformation of a group on its steric properties. That conformation plays a significant role in determining the steric effect of a group is well documented.[3,16] This is clear from the observation that the steric effects of some groups are levelled off by conformational preference. For example, though $CH_2CH_2CH_3$ is much smaller than $CH_2(CH_2)_3Ph$, their steric effects are almost the same.[10] This is because the latter group takes up such a conformation with respect to the reaction centre that it essentially exerts the same steric effect as the *n*-Pr group. It should be mentioned that conformational preference is reflected also in the work of Fujita *et al.*[17] on the additivity of the steric parameters in an unsymmetrical group. Thus it is evident that conformational effects should be kept in mind whilst developing a steric parameter.

An inorganic counterpart of the steric parameters in organic chemistry is the 'cone angle'. The concept was first introduced by Tolman in 1970 in order to quantify the steric effect of the phosphines.[18] The cone angle is defined as the angle of the cone within which a molecule can be enclosed keeping the apex of the cone at a certain distance from the interacting atom. For phosphines, this distance is chosen as the average metal–phosphorous bond length. Subsequently the concept has been extended to other inorganic ligands to estimate their bulk in connection with their steric effect.[19a] Some modifications of the concept have also been attempted.[20] Earlier we have indicated[21] from topological considerations that a cone angle can be defined for an alkyl group also. In this paper we report the measurements of the cone angle (θ_R) for a number of alkyl (R) groups.

CALCULATIONS OF THE CONE ANGLE θ_R

The coordinates of the constituent atoms of the groups in Table 1 were found out from the idealised tetrahedral geometries of the corresponding alkane with bond lengths calculated with the covalent radii of the various atoms as found in the Corey–Pauling–Koltun (CPK) precision molecular models. A sphere of radius *r* (Van der Waals' radius) was drawn around the atom, Z, determining the cone angle. From Figure 1, where P is the apex of the cone, Q the atom interacting with the reaction centre and PP′ the line whose locus generates the cone of angle θ_R, it follows that if $\angle QPZ = \theta_1$ and $\angle ZPP' = \theta_2$, $\theta_R/2 = \theta_1 + \theta_2$. For θ_1 and θ_2 we can write

$$\theta_1 = \cos^{-1}((\vec{PQ} \cdot \vec{PZ})/(|\vec{PQ}||\vec{PZ}|)) \qquad (2)$$

$$\theta_2 = \sin^{-1}(r/|\vec{PZ}|) \qquad (3)$$

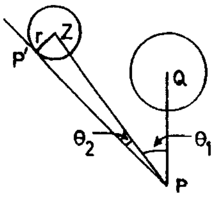

Figure 1. Illustration for the calculation of the cone angle by equations (2) and (3)

For the alkyl groups we have placed the apex of the cone (i.e. the point P in Figure 1) at a distance of 1·54 Å, the average C–C single bond length, from the interacting carbon atom. The Van der Waals' radii of the various atoms were again taken as found in the CPK models. For the groups with no phenyl ring we have used staggered (with respect to the reaction centre–α-carbon bond) conformations. The θ_R of an unsymmetric group was calculated by following the method of Tolman.[18] In case of the CPh_3 group a propeller-like conformation (Figure 2), as found in 1,1,1,3,3,3-hexaphenylpropane,[22] was used for calculating the cone angle. For $CMePh_2$ and $CEtPh_2$ the same relative orientation of the phenyl rings were used. Since the cone angles of the phenyl-substituted alkanes are quite sensitive to the orientation of the phenyl ring, we have restricted ourselves to CPh_3, $CMePh_2$ and $CEtPh_2$ only. For comparison we have calculated the cone angles (θ_P) for several phosphines using the

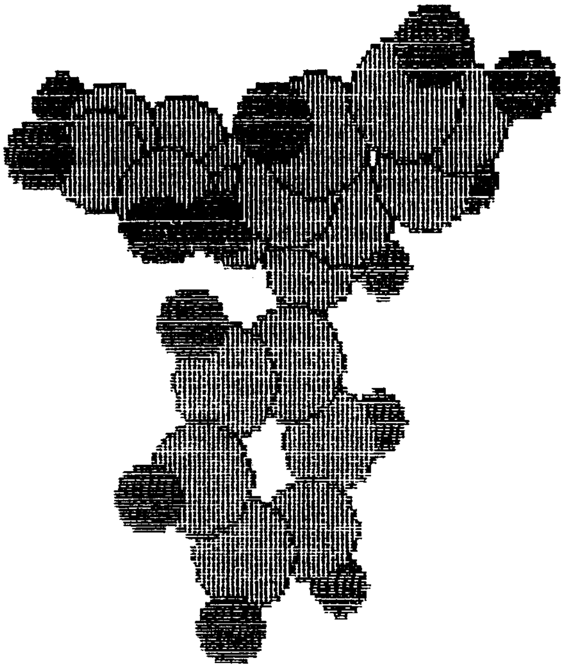

Figure 2. The propeller-like conformation of $CHPh_3$ used for the calculation of θ_R of the CPh_3 group. Larger circles represent the C atoms and the smaller ones the H atoms

Table 2. Cone angle (θ_R) data for some phosphines

No.	Phosphine	θ_P (degrees) This work	θ_P (degrees) Ref. 14
1	PH_3	88	87
2	PF_3	103	104
3	PMe_3	120	118
4	$PHPh_2$	127	128
5	$PMePh_2$	138	136
6	PPh_3	147	145
7	$PEtPh_2$	155	140
8	PEt_3	169	132

geometries of the corresponding CPK models; these are given in Table 2. The accuracy of Tolman's measurements is remarkable. However, our θ_P value for PEt_3 does not agree with that of Tolman (*vide infra*).

For single atom groups like H and the halogens, the cone angles (θ) were determined by drawing a right circular cone around the atom. The radius of the circular base was taken as the Van der Waals' radius (r) of the atom. The apex of the cone was kept at a distance d which is equal to the sum of the covalent radii of the atom and single bond carbon. The data for the various radii were taken as found in the CPK models. The calculations were done by using equation (4). The same method was applied to the CN group also.

$$\theta = 2 \tan^{-1}(r/d) \qquad (4)$$

CONE ANGLE AND OTHER STERIC SCALES

We have observed a severe limitation of the cone angle approach. It was found that in the staggered conformations the cone angles of CEt_3, $C(i\text{-Pr})_3$ and $C(t\text{-Bu})_3$ are the same. However, Tolman has reported considerably different cone angles for PEt_3, $P(i\text{-Pr})_3$ and $P(t\text{-Bu})_3$, presumably because he has used different conformations for these phosphines (with respect to the metal–phosphorous bond). Incidentally Tolman has used a staggered conformation for PMe_3 for which our measurement reproduces his data (Table 1). According to our observations, if we assume staggered conformations in Tolman's approach the cone angles of the three phosphines mentioned cannot be distinguished properly. This has restricted our study to a few types of alkyl groups (Table 1). In fact we cannot account for the change in the bulk of a group due to the branching at the β-carbon – only straight-chain alkyl substituents at the α-carbon can be accommodated in Tolman's approach.[18] The θ_R values for various alkyl groups which could be measured are given in Table 1. For ready comparison the corresponding E_s and E_s' values are also given in Table 1. In general the θ_R of an alkyl group is larger than the θ_P for the similarly substituted phosphine since in our case

$$|\overrightarrow{PQ}| = 1{\cdot}54\ \text{Å}$$

and for phosphines Tolman used

$$|\overrightarrow{PQ}| = 2{\cdot}28\ \text{Å}.$$

A rather surprising feature of our results is that the steric effect of all the halides should be more or less same as their θ_R values (Table 1) while the expected order of their steric effect is F < Cl < Br < I. This may be another drawback of our approach.

The conformational levelling of the steric effect has been discussed in an earlier section. The measurement of the θ_R of a particular group has been carried out according to the prior knowledge of its E_s or E_s' parameter. For example, we find that, since the E_s values of CH_2Et and $CH_2(n\text{-Pr})$ are almost the same, to measure θ_R of the C—(n-Pr) fragment we have to use a conformation as shown in Figure 3(a) rather than that in Figure 3(b). It should be noted that the θ_R is much larger in Figure 3(b) than in Figure 3(a). More examples of such cases can be found in Table 1.

To establish a correspondence between θ_R and the existing steric parameters, E_s and E_s', we have examined their correlations. We have found that for some 46 groups in Table 1, Taft's E_s scale correlates linearly with θ_R only to a satisfactory extent (correlation coefficient = 0·905). The significant deviants are the four halides and the two charged groups $CH_2NH_3^+$ and $CH_2CH_2HN_3^+$. If we exclude these, a very good linear correlation between θ_R and the E_s scale (equation (5); Figure 4; correlation

$$E_s = 4{\cdot}941 - 0{\cdot}041\theta_R \qquad (5)$$

coefficient = 0·950) is obtained. In Dubois' scale, data are not available for the halides and the two charged groups. For some 38 groups in Table 1 linear correlation between Dubois' E_s' scale and θ_R is satisfactory (correlation coefficient = 0·943); however the correlation improves if we exclude the CEt_3 group (equation (6);

$$E_s' = 5{\cdot}400 - 0{\cdot}044\theta_R \qquad (6)$$

Figure 5; correlation coefficient = 0·953). The reasons for the deviations of the various groups in Figures 4 and 5 are not clear. As discussed earlier there seems to be a problem in measuring the cone angles of the halides. In case of the two charged groups it is possible that the kinetically determined steric parameters contain some amount of extraneous effects (e.g. electronic, solvation, etc.).

It is very difficult to say which one of the two scales, E_s and E_s', is better. While Taft's E_s scale has been applied quite successfully in a variety of situations, there are cases where Dubois' E_s' scale yields better results.[23] However, both the scales are based on the

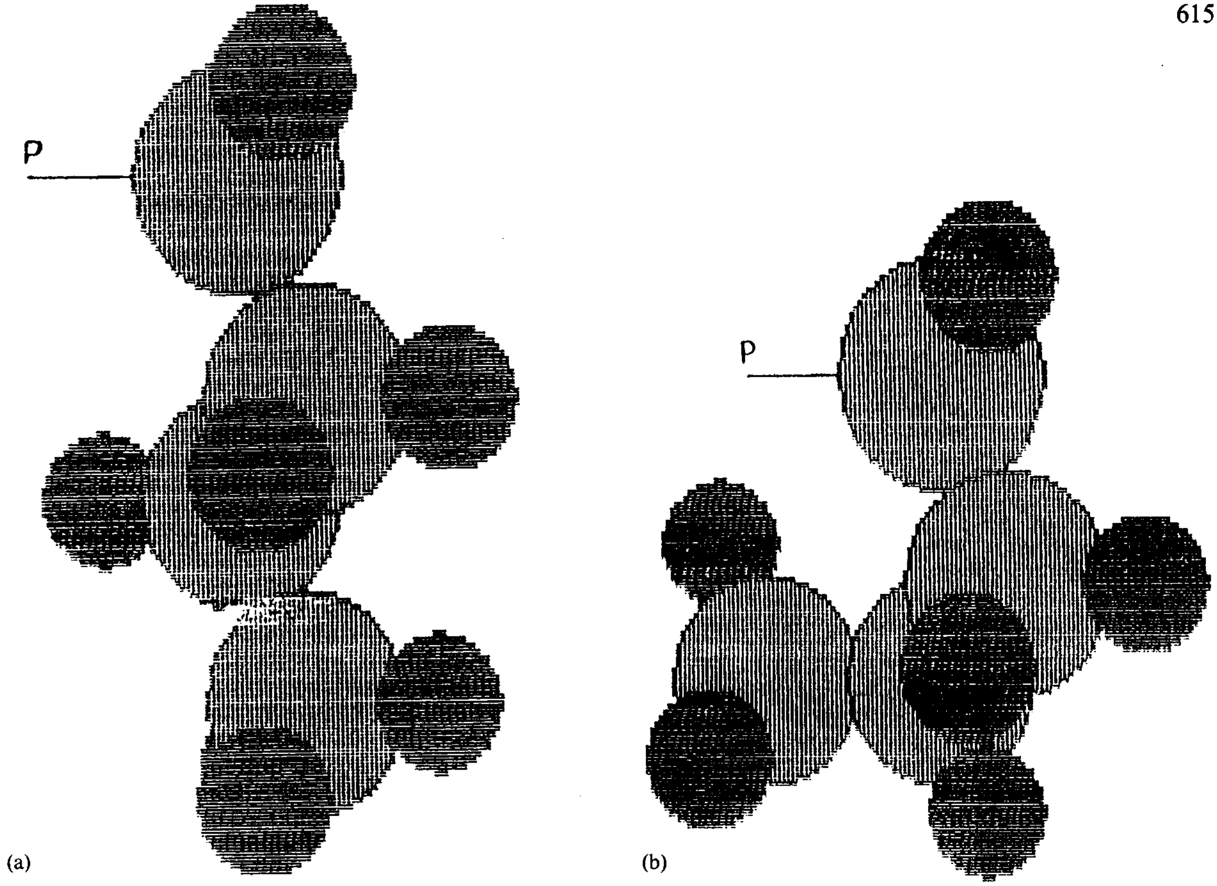

Figure 3. (a) Correct and (b) incorrect conformations of $CH_2(n\text{-}Pr)$ for measuring the θ_R of the C—(n-Pr) fragment. The point P indicates the apex of the cone; the C atoms are shown by larger circles and the H atoms by smaller circles

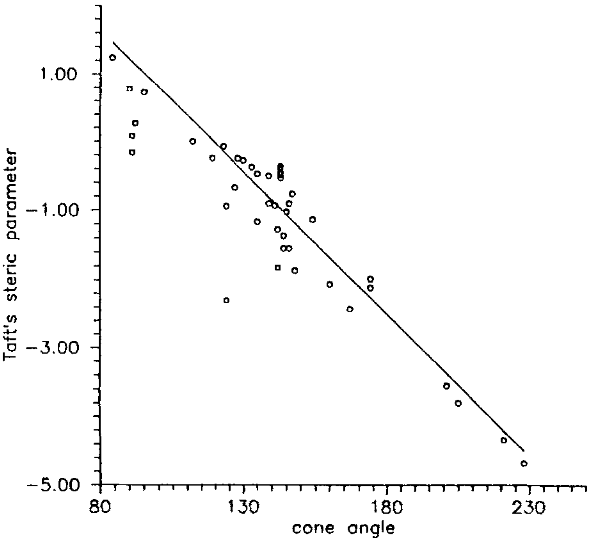

Figure 4. Correlation of Taft's E_s scale with θ_R (see Table 1 for data); points marked by the squares are not included for the least squares fit (see text). Correlation coefficient = 0.950

Taft–Ingold hypothesis. As mentioned earlier several workers have tried to modify the numerical values[4,7] of the E_s scale because of the possible role of the electronic factors of the R group in determining the rate of the acid-catalysed hydrolysis of the ester RCOOEt. Here we have applied Tolman's concept of the cone angle to an R group to measure its steric effect. Since our θ_R is determined purely from the structural features of an alkyl group, it can be assumed that θ_R does not contain any electronic component unless the electronic effect of an R group is a function of θ_R. Thus within the limitations of our approach the present linear correlations of θ_R with E_s and E_s' show that the acid-catalysed ester hydrolysis is controlled mostly by the steric effects, which is the basic assumption of the Taft–Ingold hypothesis. Incidentally Charton[8] has expressed the view that the various numerical corrections to E_s are unnecessary. However, it should be remembered that the steric effect and the electronic effect cannot be separated completely from each other. For example,

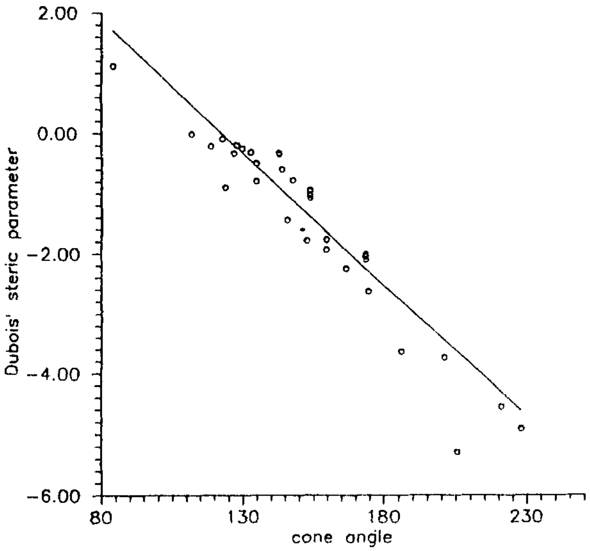

Figure 5. Correlation of Dubois' E_s' scale with θ_R (see Table 1 for data); the CEt_3 group marked by a square is not used for the correlation (see text). Correlation coefficient = 0·953

the steric strain (back strain) in $NR^1R^2R^3$ changes the hybridisation of N from sp^3 to sp^2, decreasing the basicity of the amine,[19b] and elsewhere we have shown[24] that the steric strain in the CMe_3 group leads to a value of its electronegativity higher than the expected one.

AN APPLICATION OF θ_R

One of the assumptions of the Taft–Ingold hypothesis is that in the base-catalysed hydrolysis of the esters RCOOEt the R group exerts its electronic effect in addition to the steric effect. Accordingly Taft has formulated another scale σ^* as a measure of the electronic effects of the R group by equation (7) where the

$$\sigma^* = [\log(k/k_0)_{\text{base}} - E_s]/2{\cdot}48 \qquad (7)$$

factor of 2·48 is somewhat arbitrary.[5] Recently we have shown[25] that the σ^* of a chemical group is related to its electronegativity (χ^H) in Huheey's scale.[26] We now demonstrate the use of θ_R in assessing this aspect of the hypothesis. For this purpose we examine the correlation of $\log(k/k_0)_{\text{base}}$ with θ_R and χ^H (Table 1). For some 24 groups (Table 1) the correlation coefficient is found to be 0·941 which increases significantly to 0·971 if the halogens, for which our approach seems to have problems (*vide supra*), are excluded (equation 8). Since χ^H of an R group is

$$\log(k/k_0)_{\text{base}} = -5{\cdot}502 + 5{\cdot}146\chi^H - 0{\cdot}050\theta_R \qquad (8)$$

derived from the electronegativity and hardness of the constituent atoms,[25] it measures purely the electronic effect of the group. Here we have shown that θ_R indicates only the steric effect of an R group. Hence apart from showing the applicability of the cone angles, the extent of correlation achieved by our equation (8) independently substantiates the fact that the base-catalysed hydrolysis of RCOOEt is mostly governed by the electronic and steric effects of the R group.

CONCLUSIONS

It is evident that the cone angle θ_R can also be used as a steric parameter for an alkyl group. Here it has been shown that the measurement of the relevant cone angle of a group is fairly simple. The conformational levelling of the steric effect can be easily visualised from the cone angle approach. However, the branching at a β-atom could not be accommodated. It is worthwhile mentioning that Charton[27] has felt that 'no one set of steric parameters for alkyl groups will work for all types of reactions'. Nevertheless we have shown that θ_R can be used to explain the variation in the rate constant of the base-catalysed hydrolysis of RCOOEt, the key reaction for the origin of E_s and σ^*, with R. Thus our present study, within the various limitations of our approach, independently supports the general idea of the Taft–Ingold hypothesis that, while the base-catalysed ester (RCOOEt) hydrolysis is governed mostly by the steric and electronic effects of the alkyl group, the acid-catalysed one is controlled almost solely by the steric effect.

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