STERIC EFFECTS—I

A CRITICAL EXAMINATION OF THE TAFT STERIC PARAMETER—Eₛ. DEFINITION OF A REVISED, BROADER AND HOMOGENEOUS SCALE. EXTENSION TO HIGHLY CONGESTED ALKYL GROUPS

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Abstract—The basic assumptions used in obtaining the Taft Eₛ scale of steric parameters have been examined critically. Certain inconsistencies in the existing scale are pointed out which motivate a rigorous recalculation of the scale based on a single defining reaction: the acid catalysed esterification of carboxylic acids in MeOH at 40°. This revised Taft scale is termed E_s'. The scale includes 44 of the original groups cited by Taft with 50 additional values obtained from literature data and has been extended to extremely hindered alkyl groups (13 in number) by measurement based on competitive reactivity. The complete scale from its least hindered group (H, E_s' = 1.12) to its most hindered (t-BuPr^{i}MeC-, E_s' = −7.56) spans more than eight powers of ten. A definite levelling effect has been observed in the region of $E_s' \sim -6$ and an inversion effect in two cases (i-Pr$_3$C- and t-BuPr^{i}EtC-). Some currently used quantitative approaches to steric effects are discussed and compared in the light of the E_s' scale. The corrected steric parameters, E_s^c and E_s°, have been shown not to be of general applicability and the use of the van der Waals radius relative to hydrogen subject to limitation.

The development of a quantitative measure of steric effects necessitates the use of a model system which may be theoretical or empirical. Insofar as the interest of a steric parameter concerns mainly the analysis of reactivity changes in series of closely related compounds the most fruitful approach would be a linear free energy parameter calculated from a suitably chosen reaction system. A choice of such a system, which is by no means self-evident, was advanced by Ingold some time ago.[2] Taft[3] took up Ingold's suggestion and used it to define quantitatively the well-known parameter Eₛ. To do this he used the existing rate data for four closely related reaction systems involving acid catalysed ester hydrolysis and esterification of carboxylic acids at 25° and calculated a scale of steric parameters from average values of log (k/k_0) and the following equation:

$$E_s = \log (k/k_0) \qquad (1)$$

where k_0 refers to Me, the reference substituent. Since the appearance of the original papers a certain number of authors,[4,5] recognizing the importance of the quantification of the steric effect, have turned their attention to an analysis of the basic Taft-Ingold hypothesis and the steric constants derived therefrom.

Taft pointed out the importance of a relationship between the Eₛ of a group and its van der Waals radius but failed to consider this point in detail.[3] Charton[6] has shown that, for single atom groups and symmetrical groups of the form A₃B, there is an excellent linear correlation between the van der Waals radius and Eₛ. This approach is, however, too simplistic to be of general applicability but it does indicate that the Eₛ parameter is free of electronic effects.

Several authors have maintained that the Taft Eₛ scale does not represent a complete separation of steric and polar effects and have attempted to improve upon matters in various ways. Thus Hancock[7] and, independently, Palm[8] concluded that the Eₛ contains a contribution due to hyperconjugation which has to be removed in

order to obtain true steric constants. They proposed scales of "corrected" steric constants, E_s^c and E_s° respectively.

The existing scale of steric effects has been criticized on several occasions by Shorter[4] and Charton[6] who point out inconsistencies in the calculation technique used. In our opinion the Taft Eₛ scale is in need of a closer look, both in terms of the existing values and in the experimental determination of new steric constants. It is futile to persist in a detailed examination of the existing Taft Eₛ scale since minor effects may be masked by the purely numerical failings of the existing values. This rather tedious task must be undertaken if steric effects are to be properly understood. In this regard emphasis must be placed on the fundamental Taft-Ingold hypothesis and the correct procedure for obtaining a homogeneous scale of steric effects therefrom.

In this article, we propose: (a) to examine the method used to calculate the Eₛ scale. We shall see that there is room for improvement. This will motivate a rigorous definition and a recalculation of the scale. (b) To present some newly measured steric constants which fill in the gaps in the recalculated scale as well as extend it to extremely hindered groups. (c) And to compare and evaluate currently used steric effect scales.

Revised Taft steric constants—E_s'

(a) *The Taft Eₛ scale—a closer look.* The essential Taft-Ingold hypothesis is that the acid catalysed hydrolysis of esters is controlled by steric effects, all others being equal. The soundness of this assumption was demonstrated by Taft[3] for the most unfavorable of cases, i.e. small yet rather polar groups. It follows that the assumption is also sound for other groups. The correctness of this assumption is something that we do not question. What is open to question, in our opinion, is the manner in which this assumption was exploited to generate a steric effect scale. The calculation method lacks rigor and the result lacks coherence, as a consequence.

In his original papers Taft used four closely related reactions to define a basic set of E_s values:

(i) Hydrolysis of ethyl esters in 70% v/v acetone at 25°;

(ii) Esterification of carboxylic acids in MeOH at 25°;

(iii) Esterification of carboxylic acids in EtOH at 25°; and

(iv) Hydrolysis of ethyl esters in 60% v/v aqueous acetone;

All four reactions are acid catalysed. *Assuming that these four reactions have the same sensitivity to changes in the steric effect*, Taft calculated average E_s (i.e. log (k/k_o)) values. This assumption is gratuitous and introduces an important source of error. The correct procedure is to choose a *single* reference reaction.

In addition, Taft used results furnished by Newman[9] corresponding to esterification in methanol at 40° without taking into account the difference between the sensitivity of the reaction to changes in steric effects at 25° and this temperature, i.e. the variation of δ in eqn (2):

$$\log(k/k_o) = \delta E_s \qquad (2)$$

A further difficulty with the E_s scale as reported by Taft, apart from his use of average values, is the fact that certain values for highly hindered alkyl groups appear to be contradictory. For example, the reported E_s values for the groups t-BuMe$_2$C– and t-Bu(t-BuCH$_2$)MeC– are, –3.9 and –4.0 respectively, suggesting that replacement of a Me by a neopentyl subgroup scarcely alters the steric effect. Surely one or both of these values is in error.

In order to gain some insight into this problem we have carried out a topological analysis[10] on the available data for alkyl groups. This approach pointed out that the E_s values attributed to the groups Et$_3$C– and t-BuMe$_2$C– cannot be included in the same correlation as the remaining alkyl groups. This discontinuity may be a real phenomenon which we were at pains to explain, or, more simply, the result of experimental error. New measurements (reported herein) were necessary to settle this question.

(b) *Homogeneous scale of steric parameters*—E_s'. In view of the rather fundamental and widespread interest in a reliable scale of steric effects we decided to recalculate the scale using a rigorous procedure. Indeed, the mere fact that we envisaged experimental measurements necessitated the use of a precise operational definition of

the steric effect. To do this *we chose as reference reaction the acid catalysed esterification of carboxylic acids in MeOH at 40°*, i.e. the δ of eqn (2) is equal to unity, by definition, for these conditions. An intrinsic assumption, of course, is the constancy of reaction mechanism irrespective of the nature of the carboxylic acid. This is a very convenient reference reaction, since abundant experimental data exist for these conditions, allowing the calculation of a rather large basic set of steric constants, which we denote as E_s' for the sake of clarity. The evaluation of new E_s' values may then be carried out by measurement directly on the reference reaction. It is also possible, and sometimes more convenient, to use the basic set of E_s' values to estimate the δ for reactions other than the reference reaction and to calculate new E_s' values accordingly. Of course, this is now standard procedure.

The complete results are presented in Tables 1 and 2, which include 19 E_s' determinations, of which 6 are used to verify important existing values and 13 are entirely new. These latter extend the scale to highly hindered alkyl groups. Table 1 lists the E_s' values for 94 groups. In this table we give the E_s' values for 44 of the original groups cited by Taft along with the differences between E_s and E_s', as well as values for 50 additional groups calculated from the available literature. Because preliminary competition experiments between t-BuMeCHCO$_2$H and t-BuMe$_2$CCO$_2$H showed a reactivity difference greater than calculated on the basis of the Taft E_s, it was necessary to remeasure the esterification rates of both these compounds by a direct kinetic method. The rate determined for t-BuMeCHCO$_2$H agrees within 2% with the value reported by Newman[9], whereas that for t-BuMe$_2$CCO$_2$H differs by 1.5 log units. Five other groups have been measured by competition experiments relative to the group t-BuMeCH– (t-Bu, t-BuCH$_2$–, Et$_2$CH–, EtMe$_2$C– and i-PrEtCH–) and are found to have E_s' values which agree to within ±0.02 units of those based on the data of Smith[11] Newman[9] and Chapman[12].

Bowden et al.[13] have reported E_s values for certain aromatic groups from the rates of esterification in methanol at 60°. To convert these results to E_s', i.e. esterification at 40°, we have taken into account the variation of δ with temperature. Smith's results for estification at 20°, 30°, 40° and 50° allow an estimation of δ at 60° (0.953) and E_s' values are calculated accordingly. These values are included in Table 1. Whenever we have

Table 1.

N°	R	$-E_s$ (Taft)	$-E_s'$	Δ	Source
1	H	–1.24	–1.12	–0.12	a
2	Me	0.0	0.0	–	–
3	Et	0.07	0.08	–0.01	a
4	Pr	0.36	0.31	0.05	a
5	n-Bu	0.39	0.31	0.08	a
6	i-Pr	0.47	0.48	–0.01	c

Table 1 *Contd.*

N°	R	− E_S (Taft)	− E_S'	Δ	Source
7	s–Bu	1.13	1.00	0.13	d
8	i–Bu	0.93	0.93	0.00	d
9	t–Bu	1.54	1.43	0.11	b,k
10	Et_2CH-	1.98	2.00	− 0.02	b,k
11	$EtMe_2C-$		2.28	−	j,k
12	i–PrEtCH–	−	3.23	−	d,k
13	$t-BuCH_2-$	1.74	1.63	0.11	d,k
14	t–BuMeCH–	3.33	3.21	0.12	d,k
15	$n-C_5H_{11}$	0.40	0.31	0.09	a
16	$s-BuCH_2-$	−	0.97	−	b
17	$n-Pr_2CH-$	2.11	2.03	0.08	b
18	$n-Bu_2CH-$	−	2.08	−	b
19	$i-Bu_2CH-$	2.47	2.38	0.09	b
20	$i-PrCH_2CH_2-$	0.35	0.32	0.03	d
21	$t-BuCH_2CH_2-$	0.34	0.33	0.01	d
22	$t-BuCH_2MeCH-$	1.85	1.81	0.04	d
23	$t-BuCH_2Me_2C-$	2.57	2.48	0.09	d
24	$(t-BuCH_2)_2CH-$	3.18	3.06	0.12	d
25	$i-BuCH_2CH_2-$	−	0.31	−	r
26	n–PrMeCH–	−	1.02	−	r
27	n–BuMeCH–	−	1.06	−	r
28	PrEtCH–	−	2.00	−	r
29	n–BuEtCH–	−	2.03	−	r
30	$cyclo-C_3H_5$	−	1.09	−	r
31	$cyclo-C_4H_7$	0.06	0.03	0.03	r
32	$cyclo-C_5H_9$	0.51	0.41	0.10	r
33	$cyclo-C_6H_{11}$	0.79	0.69	0.10	l
34	$cyclo-C_7H_{13}$	1.10	0.92	0.18	r
35	$cyclo-C_8H_{11}CH_2-$	0.98	0.89	0.09	m

Table 1 *Contd.*

N°	R	− E_S (Taft)	− E_S'	Δ	Source
36	cyclo-$C_6H_{11}CH_2CH_2$−	−	0.34	−	■
37	cyclo-$C_6H_{11}(CH_2)_3$	−	0.36	−	■
38	Ph	−	2.31	−	e, o
39	PhCH₂−	0.38	0.39	− 0.01	f
40	PhMeCH−	1.19	0.90	0.29	g
41	PhEtCH−	1.50	1.32	0.18	■
42	Ph₂CH−	1.76	1.50	0.26	f
43	Ph₂MeC−	−	3.73	−	f
44	Ph₂EtC−	−	4.55	−	f
45	Ph₃C−	−	4.91	−	f
46	Ph₂CH₂CH₂−	0.38	0.35	0.03	a
47	Ph(CH₂)₃	0.45	0.34	0.11	a
48	Ph(CH₂)₄	−	0.33	−	a
49	2-furyl	−	2.63	−	n
50	3-furyl	−	2.33	−	n
51	2-furylCH₂−	−	0.34	−	n
52	3-furylCH₂−	−	0.74	−	n
53	O-tolyl	−	2.82	−	o
54	O-EtC₆H₄	−	2.97	−	p
55	O-PrC₆H₄	−	3.04	−	p
56	O-PhC₆H₄	−	3.01	−	p
57	PhCH₂MeCH−	−	0.44	−	r
58	Fl‡CH	−	1.15	−	f
59	FlCMe	−	1.81	−	f
60	FlCEt	−	2.07	−	f
61	FlCPr^i	−	3.46	−	f
62	FlCBu^t	−	4.32	−	f
63	FlCPh	−	3.23	−	f

‡ Fl = fluorenyl; ‡ An = Anthracenyl

Table 1 *Contd.*

N°	R	$- E_S$ (Taft)	$- E_S^c$	Δ	Source
64	AnCH	–	1.35	–	f
65	FH₂C–	0.24	0.20	0.04	h
66	F₂HC–	0.67	0.32	0.35	v
67	F₃C–	1.16	0.78	0.38	u
68	ClH₂C–	0.24	0.18	0.06	h
69	Cl₂HC–	1.54	0.58	0.96	h
70	Cl₃C–	2.06	1.75	0.31	i
71	BrH₂C–	0.27	0.24	0.03	i
72	Br₂HC–	1.86	0.76	1.10	v
73	Br₃C–	2.43	2.14	0.29	i
74	IH₂C–	0.37	0.30	0.07	i
75	I₂HC–	–	0.93	–	v
76	I₃C–	–	2.62	–	u
77	BrMe₂C–	–	1.77	–	i
78	Br₂MeC–	–	1.92	–	i
79	Me₃Si–	–	1.79	–	u
80	F	–	– 0.57	–	u
81	Cl	–	0.02	–	u
82	Br	–	0.22	–	u
83	I	–	0.50	–	u
84	NCCH₂–	–	0.89	–	t
85	PhOCH₂–	0.33	0.32	0.01	p
86	HOCH₂–	–	– 0.03	–	q
87	CH₃(CH₂)ₙC(OH)*	–	0.35	–	q
88	CH₃(CH₂)ₙCO*	–	0.52	–	q
89	CH₃(CH₂)ₙC(OMe)H*	–	1.39	–	q
90	CH₂=CH–	–	2.07	–	q
91	CH₂=CH-CH₂–	–	0.31	–	q
92	CH₂=CH(CH₂)ₙ**	–	0.43	–	q

* n > 1
** n > 2

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Table 1 Contd.

N°	R	$-E_S$ (Taft)	$-E_S'$	Δ	Source
93	$\phi C \equiv C-$	-	1.97	-	a
94	$CH_3C(OH)H-$	-	- 0.08	-	q

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u Calculated from correlation $E_S' = -2.089 \, r_{v,min} + 3.640$ for groups H, Me, t-Bu, CCl$_3$, CBr$_3$ r = 0.9999$_3$, ϕ = 0.015 for $r_{v,min}$, cf. ref. 6.

v Calculated from correlation $E_{S,CX_nR_{3-n}}' = a \, E_S' \, CMe_nH_{3-n} + b$.

w Of the E_S' values reported here 36 were calculated from rate data for esterification in MeOH at 40° (a,b,c,d,e,l,m,n,o,s) i.e. the reference reaction ; a further 18 refer to the same reaction at temperatures other than 40° (f,j,p,s) ; the remaining values are based on data for different media and related to the reference reaction by correlation.

determined esterification rates at temperatures other than 40°, the E_S' values have likewise been calculated from a knowledge of δ at the corresponding temperature. Smith's results show that this procedure is justified.

A glance at Table 1 shows that the more reliable E_S' and the original E_S values differ at times only slightly; but in certain cases, especially for halogen containing groups, rather significantly. In effect, 12 groups differ by only 5%, 14 by from 5 to 10% and 27 by greater than 10%.

(c) *Hindered alkyl groups.* Table 2 lists the E_S' values for 13 moderate to extremely hindered alkyl groups determined in this work.

Of the E_S' values given in Table 2, two are seriously in conflict with previous E_S values reported by Taft: the E_S' of t-BuMe$_2$C- = -5.40 (E_S = -3.9) and the E_S' of Et$_3$C- = -5.29 (E_S = -3.8). The E_S value attributed to t-BuMe$_2$C- does seem anomalous when one considers the series t-BuCH$_2$- (E_S = -1.65), t-BuMeCH- (E_S = -3.33) and t-BuMe$_2$C- (E_S = -3.90) where it is seen that the effect of adding a second Me group is surprisingly small. When the E_S of the group t-Bu(t-BuCH$_2$)MeC- (-4.0) is compared with that of t-BuMe$_2$C-, the former appears

anomalous since it implies that the effect of replacing a Me by a neopentyl sub-group is practically negligible (0.1 E_S units). In our opinion the three E_S values for the groups t-BuMe$_2$C-, Et$_3$C- and t-Bu(t-BuCH$_2$)MeC- are based on faulty experimental data, due probably to the difficulty of correcting for reaction of the catalyst (HCl) with the solvent (MeOH) for very slow esterifications. The E_S' values reported in this work were obtained by a combination of direct and competition experiments using a catalyst which does not react with methanol, p-toluenesulfonic acid.

We can show that the E_S' of the group Et$_3$C- is not anomalous by means of an analogy between the effect of the replacement of the hydrogens of the Me group by Me and Et sub-groups, expressed as the following equation:

$$E_S'(CEt_nH_{3-n}) = a E_S'(CMe_nH_{3-n}) + b,$$
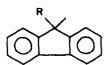
$$n = 0, 1, 2, 3 \quad (3)$$

The correlation[14] obtained on four values is excellent (r = 0.999, Ψ = 0.064) supporting the validity of the E_S' for Et$_3$C-.

Table 2. Newly measured E_S' values for hindered alkyl groups[d]

	R	$-E_S'$	Method of Measurement
95	i-PrMe$_2$C-	3.54	a
96	i-Pr$_2$CH-	5.01	b
97	Et$_3$C-	5.29	c(96,99)
98	t-BuMe$_2$C-	5.40	b
99	i-PrEt$_2$C-	6.20	c(98,100,101,102,103,104)
100	i-Pr$_2$MeC-	7.38	c(99,102,105)
101	i-Pr$_2$EtC-	7.38	c(99,102,105)
102	i-Pr$_3$C-	6.73	c(100,101,103,104,105)
103	t-BuPr^{i}CH-	6.53	c(98,99,104,105)
104	t-Bu$_2$CH-	6.97	c(102,103,105,106,107)
105	t-BuPr^{i}MeC-	7.56	c(101,104,106,107)
106	t-BuEt$_2$C-	7.21	c(104,105)
107	t-BuPr^{i}EtC-	6.62	c(104,105)

a Competition experiments with t-BuMeCHCO$_2$H and i-PrEtCHCO$_2$H
b Direct kinetic experiments
c Competition experiments with groups in parentheses
d Reproducibility better than ± 0.03 E_S' units.

Another analogy may be used to demonstrate the validity of the E_S' value of the group t-BuMe$_2$C-. The analogy is between the 1-substituted fluorenyl groups

and the groups RMe$_2$C- for R = H, Me, Et, i-Pr and t-Bu. The following equation is obtained:

$$E_S'(1\text{-}R\text{-}Fl) = 0.667 E_S'(RMe_2C-) - 0.810 \qquad (4)$$

$$r = 0.99, \ \Psi = 0.200, \ R = H, Me, Et, i\text{-}Pr, t\text{-}Bu$$

demonstrating the internal consistency of the E_S' values of these two series and therefore the plausibility of the E_S' of t-BuMe$_2$C-.

Beginning with the E_S' values in the region of ca. −6 or less there appears to be a definite *levelling* effect, i.e. the trends noted for groups less hindered than this become attenuated at this point. As the steric effect increases towards very hindered groups a rather surprising *inversion* effect is noted in two distinct cases:

for

$$t\text{-}BuPr^iMeC-, \ E_S' = -7.56$$

and

$$t\text{-}BuPr^iEtC-, \ E_S' = -6.62$$

and for

$$i\text{-}Pr_2EtC-, \ E_S' = -7.38$$

and

$$i\text{-}Pr_3C-, \ E_S' = -6.73.$$

We have checked these data carefully, as described in the Experimental, and are convinced that this effect is real.

These levelling and inversion effects involve some rather intriguing questions concerning the role of conformation in determining steric effects as well as the importance of changing molecular dimensions with substitution. In a following article these topics will be treated from a variety of viewpoints including a determination of conformational energies by the empirical force field method and a determination of the crystal structure of i-Pr$_3$CCO$_2$H. We will see that conformational preference takes precedence over other effects in controlling the variation of the steric effect with substitution in the absence of important molecular distortion.

(d) *The consequences of Taft's use of average values.* As a matter of interest one can now test the validity of the use of average values by correlating the rate data of Taft's four reference reactions with the E_S' values determined from a *single* reference reaction. The following results are obtained:

(ia) Smith and Myers,[15a] $\delta = 1.3, \ r = 0.998, \ \Psi = 0.08.$
(ib) Davies and Evans,[15b] $\delta = 1.03, \ r = 0.994, \ \Psi = 0.13.$
(ii) Smith and Burn,[15c] $\delta = 1.04, \ r = 0.9997, \ \Psi = 0.025.$
(iii) Bhide and Sudborough,[15d] $\delta = 1.14, \ r = 0.999, \ \Psi = 0.10.$
(iv) Newling and Hinshelwood,[15e] $\delta = 1.14, \ r = 0.999, \ \Psi = 0.06.$

We see that the δ's for (ib), (ii), (iii) and (iv) vary only slightly ($\delta = 1.08 \pm 0.05$). The data reported by Smith and Myers do not agree with those of Davies and Evans, although both data sets correspond, in principle, to hydrolysis in 70% aqueous acetone at 25° from a variety of sources. Oddly enough, their own rate constants measured at 20° give a poorer correlation with a rather different slope ($\delta = 1.28, \ r = 0.976, \ \Psi = 0.242$). It is

probable that the results of Davies and Evans, which are similar to those of Newling and Hinshelwood for 60% acetone, are more reliable. Thus, to do Taft's treatment justice, it would seem that the use of average values, although unnecessary, need not have been a major source of error. The use of Newman's data for esterification at 40° in MeOH without considering the influence of the temperature change is, of course, incorrect.

Discussion of the relevance of hyperconjugation free parameters

We have maintained, above, that the parameter E_s' constitutes a valid measure of steric effects. An important question to consider at this point is the necessity of the so-called "hyperconjugation-free" steric constants which continue to be currently used. Hancock[7] has stated that the Taft E_s contain a contribution due to C–H hyperconjugation which must therefore be removed to obtain "true" steric constants.

He proposed a scale of corrected steric constants E_s^c obtained from the Taft E_s values using the equation:

$$E_s^c = E_s + h(n_H - 3), \quad h = 0.306 \quad (5)$$

where n_H is the number of α-hydrogens. Palm,[8] independently, proposed an equation in which he defines a steric parameter E_s^o "corrected" for C–C and C–H hyperconjugation:

$$E_s^o = E_s + 0.33(n_H - 3) - 0.13n_C. \quad (6)$$

When only alkyl groups are considered this reduces to:

$$E_s^o = E_s + 0.20(n_H - 3) \quad (7)$$

similar to the Hancock equation with a slightly different correction term.

Up to this point then we have seen the existence of four steric parameters, namely, E_s, E_s', E_s^c and E_s^o. The first two, E_s and E_s', are not distinct since E_s' is simply the Taft E_s calculated using a self-consistent procedure; the parameters E_s^c and E_s^o are derived from E_s using eqns (5) and (7). An important question is whether or not anything is to be gained by modifying the E_s' values as suggested by Hancock and Palm in the case of the original E_s values. In order to answer this question and to compare E_s' with E_s we will consider correlations using the data for four reaction series taken from the literature:

Series 1—acid catalysed hydrolysis of ethyl esters in aqueous acetone at 24.8° (Davies and Evans[15b]).

Series 2—methanolysis of β-naphthylesters at 25° catalysed by HCl (Harfenist and Balzly[16]).

Series 3—propanolysis of same.

Series 4—iso-propanolysis of same.

The parameters used in the correlations are E_s, E_s', $E_s'^c$, $E_s'^o$ and Δn ($\Delta n = n_H - 3$). The two parameters $E_s'^c$ and $E_s'^o$ are derived from eqns (5) and (7) using E_s'. Five correlations were carried out on each series using the following equations:

(A) $\log k = \delta E_s + b$
(B) $\log k = \delta E_s' + b$
(C) $\log k = \delta E_s'^c + b$
(D) $\log k = \delta E_s'^o + b$
(E) $\log k = \delta E_s' + a\Delta n + b$.

The results are given in Table 3. It may be seen that, of the four reaction series considered, the correlations with E_s' are better for Series 2–4 than with E_s while the correlation with E_s is very slightly better for Series 1. This is as expected since Taft used the data of this series

Table 3.

Series	δ	b	a	s	r	F	v	n
1 A	0.983	4.366	–	0.029	0.998	2048	0.066	9
B	1.038	4.366	–	0.046	0.996	812	0.105	9
C	0.679	4.282	–	0.101	0.979	169	0.231	9
D	0.779	4.300	–	0.076	0.988	294	0.175	9
E	0.983	4.348	0.036	0.042	0.996	421	0.103	9
2 A	1.372	0.461	–	0.106	0.992	260	0.152	6
B	1.485	0.453	–	0.066	0.997	675	0.094	6
C	0.937	0.312	–	0.079	0.996	476	0.112	6
D	1.079	0.346	–	0.051	0.998	1126	0.073	6
E	1.248	0.388	0.128	0.033	0.9993	1020	0.054	6
3 A	1.667	1.121	–	0.160	0.998	171	0.187	6
B	1.806	1.113	–	0.112	0.994	350	0.131	6
C	1.145	0.936	–	0.079	0.997	689	0.093	6
D	1.317	0.978	–	0.056	0.999	1385	0.066	6
E	1.398	0.998	0.221	0.053	0.999	585	0.072	6
4 A	1.889	2.334	–	0.203	0.985	138	0.209	6
B	2.049	2.324	–	0.147	0.992	263	0.151	6
C	1.301	2.121	–	0.093	0.997	652	0.0996	6
D	1.495	2.130	–	0.075	0.998	998	0.078	6
E	1.527	2.177	0.283	0.075	0.998	378	0.089	6

Correlation of Rate Data to Test the merits of E_s, E_s', $E_s'^c$ and $E_s'^o$.

to calculate the corresponding values of E_s. For Series 1, E_s' yields a more significant correlation than either $E_s'^0$ or $E_s'^c$. For Series 2, 3 and 4 the most significant single parameter is $E_s'^0$.

These data have also been examined using a two-parameter equation with E_s' and Δn as independent variables. For Series 1, Δn is not significant, while for the Series 2–4 the correlations are more significant in terms of E_s' and Δn than E_s' alone. This gives us the possibility of calculating the value of h, the "correction" term ($h = a/\delta$), appropriate to each series. The result is $h = 0.103$ for methanolysis, 0.158 for propanolysis, and 0.185 for iso-propanolysis. This shows that even for such closely related reactions there is no unique value of h to be used in modifying E_s'; neither 0.2 (Palm[8]) nor 0.306 (Hancock[7]) correspond to all cases. Thus, it would seem that the usefulness of defining "corrected" steric parameters is open to question. What is perhaps more revealing is the use of the two parameters E_s' and Δn together to assess their relative importance.

E_s' and the Van der Waals radius

In view of the careful preparation of the E_s' scale and the unimportance of hyperconjugation it is interesting to consider the relationship between the E_s' constants and the Van der Waals radius.

It has been shown[6] that there exists an excellent linear relationship between the Van der Waals radius of certain symmetrical groups and the corresponding E_s. In view of the subsequent criticisms levelled against the E_s scale[3] it is interesting to consider a correlation between E_s' and the Van der Waals radius, $r_{v,\,min}$, of Charton. Thus for the groups H, Me, t-Bu, CCl_3 and CBr_3, we find an improved linear relationship ($r = 0.99993$, $\psi = 0.015$) thus identifying the steric nature of the E_s' parameter.

Charton[5] has proposed a steric parameter, called ν, defined as the Van der Waals radius relative to hydrogen ($\nu_x = r_x - r_H$). Due to the conceptual difficulty of defining the Van der Waals radius for non-symmetrical groups he makes use of the same rate data as were used to calculate the E_s' scale and the following correlation equation:

$$\log k = a\nu_x + b. \tag{8}$$

In principle this equation leads to the relative radii ν_x of non-symmetrical groups that are otherwise hard to define. However this is based on the assumption that there is an excellent $\log k - r_{v,\,min}$ correlation. In fact, we have ascertained that the scope of eqn (8) cannot be extended to crowded groups even when symmetrical.

One can, for example, try to estimate an order of magnitude of the steric effect of the group $t-Bu_3C-$, making use of the electron diffraction data of Burgi and Bartell[17a,b] for $t-Bu_3CH$ and the Van der Waals radius of hydrogen, 1.20 Å. The calculated $r_{v,\,min}$ (4.24 Å) and $r_{v,\,max}$ (5.03 Å) can be used with Charton's equations in terms of E_s':

$$E_s' = -2.089 r_{v,\,min} + 3.640 \tag{9}$$
$$r = 0.9993; \ \psi = 0.015$$

$$E_s' = -1.339 r_{v,\,max} + 2.819 \tag{10}$$
$$r = 0.997; \ \psi = 0.094.$$

Thus we obtain: $E_s'(r_{v,\,min}) = -5.21$ and $E_s'(r_{v,\,max}) = -3.92$. It is to be noted that these two values are quite

different and it remains to be seen whether one of the two is confirmed experimentally. A glance at Table 2 shows that this is not the case; the experimental value of the group $t-BuPr'MeC-$ (-7.56) is already significantly greater than the estimates for $t-Bu_3C-$. Evidently Charton's model, which is so successful for slightly hindered symmetrical groups, breaks down at some point. Beyond these particular cases, interpretation of the steric effects of alkyl groups justifies a deeper analysis of the overall amplitude of the E_s' factors.

OVERVIEW

Ideally one would like to transcend the experimental determination of steric effects by means of theoretical calculations. One such approach, by De Tar,[18] attempts a calculation of the Taft steric constants using the empirical force field method. This is tantamount to calculating the free energy of activation corresponding to the reaction which defines the Taft E_s. This approach is very promising indeed but as a predictive tool must be used with some caution. One reason for this is that prior to this experimental work the higher values of E_s were considered excellent. In fact, we have shown above that the Taft E_s values for the groups Et_3C- and $t-BuMe_2C-$ are too positive by ca. 1.5 log units. Efforts to bring calculation into line with these values necessarily introduce errors. In addition, we feel that a more complex treatment of conformational preference should be considered.

The empirical force field method will, without a doubt, go a long way toward liberating the chemist from the experimental measurement of steric effects but it is, in its germinal stages, tributary to reliable experimental data. We feel that the E_s' values reported in this work provide a sound basis from which to launch such studies and hope that further work in this area will be stimulated. The complete E_s' scale, from its least hindered (H, $E_s' = 1.12$) to its most hindered group ($t-BuPr'MeC-$, $E_s' = -7.56$), spans a range of greater than 8 powers of ten, effectively demonstrating how steric effects can quite easily predominate over all others in determining reactivity.

This extended steric effect scale permits an analysis of the evolution of the steric effects of alkyl groups as a function of substitution which we will be considering in detail in a subsequent article.

Competition experiments. The rate constant determined for the esterification of t-BuMe₂CCO₂H shows that it is impracticable to consider measuring groups of comparable or greater steric hindrance by a direct method. For this reason we have chosen to measure relative rates of esterification from competition experiments.

These experiments were carried out at 50 or 100° using a mixture of two carboxylic acids in MeOH in the presence of *p*-toluenesulfonic acid. The reactions were carried out under conditions such that the extent of reaction was slight (≈ 5%). In this case, the relative reactivities may be determined from the ratio of product esters formed. This is particularly important for the very unreactive acids used in this study.

A typical competition experiment was carried out as follows: quantities of two carboxylic acids (0.0002 moles) were weighted into a glass tube to which 2 ml of 0.05M *p*-toluenesulfonic acid in MeOH were added. After dissolution of the organic acids the resulting soln was divided into three parts into small tubes that were sealed and placed into a bath thermostated at 50° or 100°, depending upon the pair of acids concerned. After a suitable time limit had elapsed, tubes were removed and treated by pouring the reaction mixture into 2 ml of 5% KHCO₃ followed by extraction with 2 ml of pentane. The pentane soln contained a mixture of the two Me esters formed, but no acid, and was analysed by glpc on a 5' SE 30-chromosorb W column using a Girdel model 75-FS-1 apparatus equipped with hydrogen flame detector and electronic integrator. In the presence of an internal standard the integrated peak areas may be converted into the number of moles of ester produced. Thus, in the case of slight reaction, for two acids I and II, the relative rate is $k_I/k_{II} = [E_I]/[E_{II}] \cdot [II]/[I]$, where E_I and E_{II} are the esters formed from the acids I and II, respectively.

In order to have reaction times that are not prohibitively long concentrations of catalyst up to and including 0.05M were used. In the competition experiments variation of catalyst concentration within these limits did not introduce a change in relative reactivities.

The accurate measurement of the relative concentrations of esters necessitates reactivity ratios that are not too different from unity. The error becomes rather serious when the ratio exceeds 1/5. It is found however that the measured relative reactivity in the case of two acids which have essentially the same reactivity, i.e. t-BuMeCHCO₂H and i-PrEtCHCO₂H, does not depend on the initial acid concentrations as long as they are held below 0.1N. This gives us the possibility of measuring rather precisely reactivity differences as large as 1/10 by modifying to initial concentrations to yield product ratios with the 1/5 limit. As shown in Table 2 the relative reactivity of a given acid has been measured, in general, with respect to a number of acids whose reactivities are not too disparate. Thus the more reactive acids have been measured relative to the less reactive ones by an overlap technique.

Product identification. The type of reaction considered here is especially well-documented and the identity of the products can be considered as known. We did however verify the glpc retention times of all products on several different columns (SE 30, DEGS, Apeizon L) with those of authentic samples prepared by the reaction of the sodium salts of carboxylic acids with MeI in HMPT.[19] The retention times agreed in all cases. In two instances however, it seemed particularly important to identify the reaction products, i.e. for the esterification of i-Pr₂CCO₂H and t-BuPrᶦEtCCO₂H, since these two compounds were found to react much faster than expected. Accordingly the mass spectra of the esterification products in methanol was recorded using a JEOL JMS-D100 mass spectrometer equipped with a JEOL JGC-20K gas chromatograph (SE 30 Column). The reaction products were in all respects identical to authentic samples.

Carboxylic acids. A number of carboxylic acids used in this study were obtained from commercial sources: t-butylacetic acid, diethylacetic acid, butyric acid, and isovaleric acid.

Di-t-butylacetic acid was prepared according to Newman's method.[20]

The remaining carboxylic acids were prepared from commercial acids by alkylation of the corresponding ethyl esters. The synthetic method is described elsewhere.[21] Hydrolysis of the hindered acids thus prepared was carried out in t-BuOK–DMSO as previously reported.[22] The carboxylic acids thus prepared exhibited NMR and IR spectral characteristics consistent with their structures and their purity was checked by neutralization equivalent measurements.

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[12] Ref j, Table 1.

[13] Ref f, Table 1.

[14] As a test for the significance of correlations we use the Ψ statistic proposed by Exner.[23] This statistic is defined as

$$\Psi = \left\{ \left[\sum (X_i - X_i')^2 \Big/ \sum (X_i - \bar{X})^2 \right] (n/n - f) \right\}^{1/2}$$

where X_i = experimental value; X_i' = calculated value; $\bar{X}$ = average value; f = number of adjustable parameters; n = number of points. Conventionally a correlation is considered as: very good for $\Psi < 0.02$; good for $\Psi \approx 0.1$; fair for $\Psi \approx 0.2$. The extreme upper limit for which an empirical relationship is valid is $\Psi \approx 0.5$. The Ψ statistic is related to the correlation coefficient r by

$$\Psi = [(1 - r^2)(n/n - f)]^{1/2}.$$

For the sake of completion we also give the F statistic.[24]

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