at 70 ± 0.5 °C with gentle stirring by means of a bar magnet, workup similar to the above procedure gave tan to brown, powdery product: mp 315–316 °C dec; yield 0.78 g (65%). The IR spectrum was identical with that of authentic HNS.[20] The presence of hydroquinone in the aqueous filtrate was detected by high-pressure LC.[21]

The products from other bases (Table IV) varied in color after the acetone wash from gray to light tan to brown: mp ~315 °C; IR spectra identical with that of authentic HNS. The yields summarized in Table III were obtained when the quantity of pyridine and the reaction time were varied as indicated. The yields obtained in reactions with air excluded are cited in Table V.

A bright orange, acetone-washed solid, mp 404–406 °C dec (acetone), was obtained from both cyclohexylamine and triethylamine. Anal. Calcd for $C_{14}H_6N_6O_{12}$ (HNS): C, 37.33; H, 1.34; N, 18.67. Found: C, 43.64; H, 1.54; N, 16.93.

Registry No. HNBB, 5180-53-0; HNS, 20062-22-0; DDQ, 84-58-2; tetrafluoro-*p*-benzoquinone, 527-21-9; *o*-chloranil, 2435-53-2; chloranil, 118-75-2; *p*-benzoquinone, 106-51-4; 2,5-diphenylbenzoquinone, 844-51-9; methyl-*p*-benzoquinone, 553-97-9; 1,4-naphthoquinone, 130-15-4; tetramethyl-*p*-benzoquinone, 527-17-3; tetrahydroxy-*p*-benzoquinone, 319-89-1; 9,10-anthraquinone, 84-65-1; *p*-nitroaniline, 100-01-6; aniline, 62-53-3; quinoline, 91-22-5; *N*,*N*-dimethylaniline, 121-69-7; pyridine, 110-86-1; 2-picoline, 109-06-8; 4-picoline, 108-89-4; morpholine, 110-91-8; cyclohexylamine, 108-91-8; triethylamine, 121-44-8.

Correlation of Activation Energies with Taft's Alkyl Inductive Substituent Constants and Its Implications to the Respective Steric Parameters. Dual Kinetic Parameter Relationships

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Fourteen sets of activation energies and four sets of steric parameters have been correlated with Taft's alkyl inductive substituent constants $\sigma_I(R)$. The correlated activation energies are from bimolecular processes either in solution or in the gas phase, polar or nonpolar, and from unimolecular decomposition reactions in the gas phase. Substitution of the E_a vs. $-\sigma_I(R)$ correlations into the Arrhenius equation leads to eq 6, where a and b are the coefficients of the linear regression equation of E_a vs. $-\sigma_I(R)$ and A is the Arrhenius preexponential factor. The function E_s' (eq 3) could be viewed as a "steric function" but does not seem to be related to any conventional steric parameter. However, the ratio $(\ln A - b/RT)/\ln k_{calcd}$, or its inverse, in certain cases is linearly related to $E_s^c(R)$ constants. Possibly the linearity between the ratio $(\ln A - b/RT)/\ln k_{calcd}$, or its inverse, and $E_s^c(R)$ indicates that the function $(\ln A - b/RT)/\ln k_{calcd}$ can separate the steric effect of the substituent, provided that the steric effect has an entropic component that dominates over the respective enthalpic component. In such a case the physical meaning of the function is "the fraction of energy attributed to the steric effect of the substituent". Combining eq 6 with the appropriate equations of the transition-state theory, one obtains eq 7. Equation 7 indicates that kinetic data that can be analyzed by eq 6 may involve the isokinetic effect. It has been noted that the various substituent constants, i.e., $E_s(R)$, υ_{OR}, and $\sigma_I(R)$, used in alternative representations of a given set of kinetic data are interrelated. This led to the conclusion that "a correlation amounts to the division of energy expressed either by E_a or by $\log (k/k_0)(\log k)$ into two (and possibly more) parts in a more or less arbitrary albeit self-consistent way". This, perhaps, is the main source of the existing controversy on the validity of $\sigma^*(R)$ and $\sigma_I(R)$ scales.

Activation energies for reactions such as nucleophilic displacements (eq 1a), alkaline hydrolysis of alkyl acetates (eq 1b), gas-phase unimolecular decomposition reactions (eq 1c), or hydrogen atom abstraction by free radicals (eq 1d) all show a marked dependence on the structure of the

$$RX + Y^- \rightarrow RY + X^- \quad (1a)$$

$$ROAc + OH^- \rightarrow ROH + AcO^- \quad (1b)$$

$$RCl \rightarrow R'_{ene} + HCl \quad (1c)$$

$$CD_3\cdot + RH \rightarrow CHD_3 + R\cdot \quad (1d)$$

substituent R. Thus, considering specifically the reaction series for R = CH_3, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, and *t*-Bu, the respective ranges in E_a's for the reactions 1a–d are 5.3[1] (X = Br, Y = Cl), 4.7,[2] 11.5,[3] and 6.2.[4] It is of interest to investigate the basis for such marked dependence of E_a on R. This problem has been stated previously but concerned mainly reactions of type 1b[5] and to a lesser extent reactions such as 1a.[6a,b]

Taft[5] has represented data of alkaline hydrolysis of esters with structural variation at the acyl or alkoxy moieties as two-parameter relationships. According to this analysis, differences in energies of activation in a given series of similar reactions are assumed to arise from differences in the polar and steric effects of the varied substituent. Charton has introduced[7-11] an alternative representation of the same data and of data from reactions such as 1a, which attributes differences in free energy of activation to primarily steric effects of the varied sub-

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(1) Hughes, E. D.; Ingold, C. K.; MacKie, J. D. H. *J. Chem. Soc.* **1955**, 3173.

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(6) (a) Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571. (b) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1969; p 548.

(7) Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 1552. Charton, M. *J. Am. Chem. Soc.* **1975**, *97*, 3694.

(8) Charton, M. *J. Org. Chem.* **1976**, *41*, 2906.

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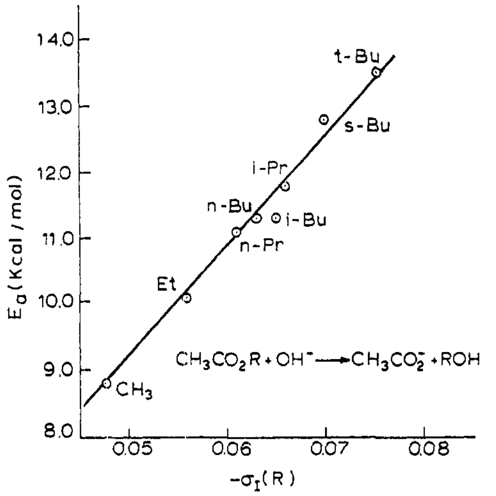

Figure 1. Plot of activation energies for alkaline hydrolysis of alkyl acetates in 70% acetone-water against Taft's $\sigma_I(R)$. The data are from ref 2 and the constants from ref 21.

stituent, with a *small, constant* polar contribution assigned to all substituents. On the basis of this analysis Charton[7] and others[12,13] for various reasons have questioned the validity of the $\sigma^*(R)$ and $\sigma_I(R)$ scales.

We have recently correlated activation energies for reactions 1a–d and steric substituent parameters with gas-phase ionization potentials of free radicals, IP(R).[14] It has been shown[14] that IP(R)'s behave like additive substituent constants and correlate closely the values of $\sigma_I(R)$. The purpose of this paper is (1) to show that energies of activation for reactions such as 1a–d are linearly related to Taft's alkyl inductive substituent constants $\sigma_I(R)$, (2) to report correlations of certain steric parameters with $\sigma_I(R)$, (3) to discuss the implications of these correlations with respect to steric effects in general, and (4) to point out a possible source of the existing controversy on the validity of $\sigma^*(R)$ and $\sigma_I(R)$ scales.

In Figure 1 activation energies for reaction 1b[2] are plotted against Taft's $\sigma_I(R)$ constants. A satisfactory linearity ($r = 0.986$) is observed. Table I summarizes similar correlations for over a dozen E_a sets. In Table I are given the type of reaction, the reaction phase, the range of the structural effect (RSE), the regression equation, the correlation coefficient, and the kind and the number of data points in the correlation. Entries 1 and 2 in Table I are correlations of E_a's for alkaline hydrolysis of esters having a constant acyl moiety and a varied alkoxy group. It is interesting to note the opposite effect of the substituent on the activation energies in acetates and formates. This can be seen by comparing either the sign of the respective RSE's or the sign of the slope in the relevant regression equation. The "changing sign" of the substituent effect and the relatively small RSE value, i.e., 1.8 kcal/mol, are rather strong indications that an isokinetic effect is operable in reaction entry 2 (Table I) and that the experimental temperatures were close to and below the isokinetic temperature.[15] Even more interesting is the correlation for entry 3 between E_a's for acid-catalyzed hydrolysis of alkyl thiolacetates and $\sigma_I(R)$. This does not seem to agree with the Taft–Ingold hypothesis that there is no polar effect in the acid hydrolysis of esters.[5] Evidently this is true for esters with structural variation at the acyl moiety only. Entries 4–8 are correlations of E_a's for typical S_N2 reactions. Entries 13–15 are examples of correlations between activation energies for hydrogen abstraction by radicals and $\sigma_I(R)$. Entries 16–18 are analogous correlations of E_a's for gas-phase unimolecular decomposition reactions. Thus the given examples of correlations cover cases of polar and nonpolar reactions, as well as reactions in the liquid and the gas phase.

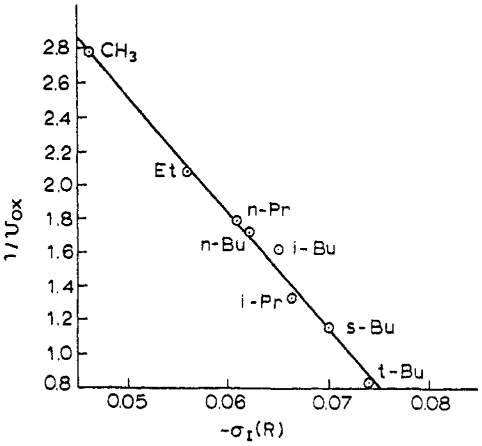

Figure 2. Plot of the inverse of Charton's υ_{OX} (X = R) steric parameters against $\sigma_I(R)$.

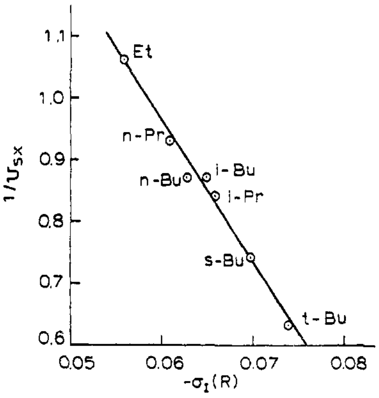

Figure 3. Charton's υ_{SX} (X = R) steric constants plotted as in Figure 2.

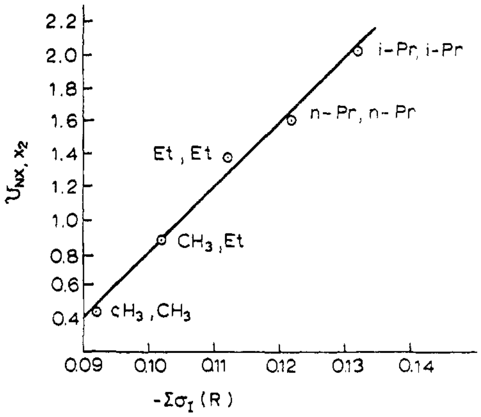

Figure 4. Charton's $\upsilon_{NX_1X_2}$ (X = R) plotted against ($\sigma_I(R_1) + \sigma_I(R_2)$).

Charton has derived[9] a set of steric substituent constants, υ_{OX}, from ester hydrolysis kinetic data (X = R in $R'CO_2R$, entry 9, Table I). These constants, when plotted against $\sigma_I(R)$, fall on a smooth curve. The inverse, however, of the constants varies linearly with $\sigma_I(R)$ (Figure 2). The analogous steric parameter υ_{SX}[11] exhibits a similar dependence on $\sigma_I(R)$ (Figure 3). In Figure 4 Charton's steric

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[12] Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

[13] Adcock, W.; Khor, T. C. *J. Org. Chem.* **1978**, *43*, 1272.

[14] Screttas, C. G. *J. Org. Chem.* **1979**, *44*, 1471.

[15] Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 325, 379.

Table I. Correlation of Activation Energies and Steric Parameters with Taft's Alkyl Inductive Substituent Constants, $\sigma_I(R)^n$

reaction	regression eq	*r*	RSE[a]	R in corr data[c]	ref
	Bimolecular Liquid Phase				
1, $CH_3CO_2R + OH^- \rightarrow CH_3CO_2^- + ROH$	$E_a = 167.239(-\sigma_I(R)) + 0.864$	0.986	−4.7	1-8	*d*
2, $HCO_2R + OH^- \rightarrow HCO_2^- + ROH$	$E_a = -63.943(-\sigma_I(R)) + 12.488$	0.995	1.8[b]	1-3, 6	*e*
3, $CH_3COSR + H_2O \xrightarrow{H^+} CH_3CO_2H + RSH$	$E_a = 132.844(-\sigma_I(R)) + 10.838$	0.993	−3.6	1, 2, 6, 8	*f*
4, $RBr + I^- \rightarrow RI + Br^-$	$E_a = 197.823(-\sigma_I(R)) + 7.234$	0.981	−5.7	1-3, 5, 6, 8	*g*
5, $RBr + Cl^- \rightarrow RCl + Br^-$	$E_a = 166.328(-\sigma_I(R)) + 7.799$	0.929	−5.3	1-3, 5, 6, 8	*g*
6, $RBr + Br^{*-} \rightarrow RBr^* + Br^-$	$E_a = 208.853(-\sigma_I(R)) + 5.724$	0.959	−6.0	1-3, 5, 6, 8	*g*
7, $RBr + S_2O_3^{2-} \rightarrow RS_2O_3^- + Br^-$	$E = 203.748(-\sigma_I(R)) + 6.380$	0.948	−5.9[b]	1-3, 5, 6	*g*
8, $RI + Cl^- \rightarrow RCl + I^-$	$E_a = 93.553(-\sigma_I(R)) + 11.659$	0.964	−2.6[b]	1-3, 5, 6	*g*
9, $R'CO_2R + H_2O \rightarrow R'CO_2H + ROH$	$1/\upsilon_{OX} = -68.845(-\sigma_I(R)) + 5.973$	0.993		1-8	*h*
10, $R'CONX_1X_2 \xrightarrow{H_2O} R'CO_2H + NHX_1X_2$	$\upsilon_{NX_1X_2} = 38.900\Sigma(-\sigma_I(R)) - 3.101$	0.994		1-1, 1-2, 2-2, 3-3, 6-6	*i*
11, $R'COSR \xrightarrow{H_2O} R'CO_2H + RSH$	$1/\upsilon_{SX} = -23.202(-\sigma_I(R) + 2.357$	0.993		2-8	*j*
12	$\upsilon_X = 37.981(-\sigma_I(R)) - 1.623$	0.929		2-8	*k*
	Bimolecular Gas Phase				
13, $RH + CD_3\cdot \rightarrow CD_3H + R\cdot$	$E_a = -204.546(-\sigma_I(R)) + 23.495$	0.948	6.2	1, 2, 4, 6-9	*l*
14, $CH_4 + R\cdot \rightarrow CH_3\cdot + RH$	$E_a = 216.964(-\sigma_I(R)) + 4.782$	0.959	−6.3	1-4, 6, 8	*l*
15, $RH + CH_3\cdot \rightarrow R\cdot + CH_4$	$E_a = -201.693(-\sigma_I(R)) + 23.777$	0.990	5.8	1, 2, 6, 8	*l*
	Unimolecular Gas Phase				
16, $RN{=}NR \rightarrow RN{=}N\cdot + R\cdot$	$E_a = -378.278(-\sigma_I(R)) + 72.649$	0.961	11.9	1, 2, 4-8	*m*
17, $RCl \rightarrow R'_{ene} + HCl$	$E_a = -623.558(-\sigma_I(R)) + 92.896$	0.940	11.5	2-8	*m*
18, $R_2Hg \rightarrow RHg\cdot + R\cdot$	$E_a = -771.849(-\sigma_I(R)) + 93.939$	0.961	21.0	1, 3, 4, 6	*m*

[a] Range of structural effect, $E_a(CH_3X) - E_a(t\text{-BuX})$, in kcal/mol. [b] Calculated by extrapolation. [c] CH_3 = 1; Et = 2; *n*-Pr = 3; *n*-Bu = 4; *i*-Bu = 5; *i*-Pr = 6; *s*-Bu = 7; *t*-Bu = 8, c-C_6H_{11} = 9. [d] Reference 2. [e] Leimm, R.; Korte, R.; Laaksonen, E.; Lehmuskoski, U., *Suom. Kemistil. B* **1946**, *19*, 93; *Chem. Abstr.* **1947**, *41*, 5370d. [f] Tarbell, D. S.; Harnish, D. P. *Chem. Rev.* **1951**, *49*, 1. [g] Taken from ref 6a. [h] From ref 9. [i] Reference 10. [j] Reference 11. [k] Reference 7. [l] Gray, P.; Herod, A. A.; Jones, A. *Chem. Rev.* **1971**, *71*, 247. [m] Reference 3. [n] $\sigma_I(R)$ values were from ref 21 [(CH_3) 0.046, (Et) 0.056, (*n*-Pr) 0.061, (*n*-Bu) 0.063, (*i*-Bu) 0.065, (*i*-Pr) 0.066, (*s*-Bu) 0.070, (*t*-Bu) 0.074] and from ref 20 [(c-C_6H_{11}) 0.062].

Table II. Attempted Separation of Steric Effect via Function 9

reaction	sign of *a*[a]	function plotted against $E_s^c(R)$	form of plot	remarks[c]
1, $CH_3CO_2R + OH^-$	+	$\ln k_{calcd}/(\ln A - b/RT)^b$	linear	
2, $HCO_2R + OH^-$	−	$(\ln A - b/RT)/\ln k_{calcd}$	linear	
3, $CH_3COSR + H_3O^+$	−		linear	*i*-Pr point above the line
4, $RBr + I^-$	+	$\ln k_{calcd}/(\ln A - b/RT)$	concave	
5, $RBr + Cl^-$	+		concave	*i*-Pr and *t*-Bu points deviating
6, $RBr + Br^{*-}$	+		concave	
13, $RH + CD_3\cdot$	−	$(\ln A - b/RT)/\ln k_{calcd}$	invariant	2.86 ± 0.09 (*n*-Bu, *i*-Bu, *i*-Pr, *s*-Bu, *t*-Bu, *c*-Hex); 2.26 (Me, Et)
14, $CH_4 + R\cdot$	+	$\ln k_{calcd}/(\ln A - b/RT)$	concave	
16, $RN_2R \rightarrow R\cdot + RN_2\cdot$	−	$(\ln A - b/RT)/\ln k_{calcd}$	linear	
17, $RCl \rightarrow R'_{ene} + HCl$	−		linear	
18, $R_2Hg \rightarrow R\cdot + RHg\cdot$	−		linear	

[a] In regression equation; see relevant entry in Table I. [b] $\ln k_{calcd}$ calculated from the appropriate regression equation and from eq 6 at T = 298.15 K. [c] For the kind and the number of the data points see relevant entry in Table I.

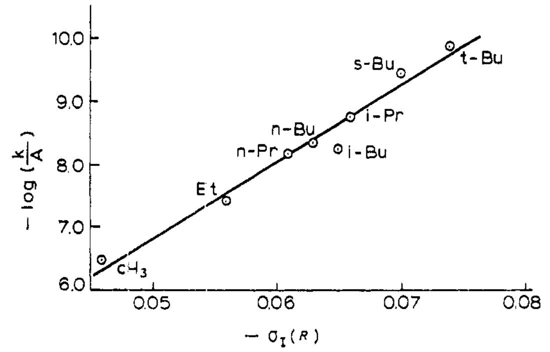

Figure 5. Plot of the negative of the logarithm of the ratio (rate constant)/(preexponential factor) for the alkaline hydrolysis of alkyl acetates in 70% acetone–water at 24.7 °C against σ_I(R). Data are from ref 2.

constant $\upsilon_{NX_1X_2}$[10] is plotted against the sum of the σ_I(R)'s of the corresponding X_1 and X_2. In another report,[14] we have shown that analogous correlations hold between the data in the Table I and gas-phase ionization potentials of free radicals. In that work an attempt was made to explain the linearity between E_a's and IP(R)'s. The explanation was based on the relationship between IP(R)'s and both homolytic and heterolytic bond dissociation energies and thus to reaction enthalpies.[14] The discussion that follows is intended to give a more satisfactory interpretation of the linearity between E_a's and σ_I(R). It is an extension of the E_a vs. IP(R) correlations.[14]

The correlations between E_a's and σ_I(R) by no means could mean that differences in E_a's within a reaction series arise by a single interaction mechanism.[16] The fact that these kinetic data appear to be representable by a single-parameter equation is rather deceiving. Replacing E_a with its equivalent from the Arrhenius equation, $E_a = -RT \ln (k/A)$, we can see that a plot of ln (k/A) against σ_I(R) should be linear. Figure 5 gives an example of such a plot. In contrast, plots of log k against $\sigma^*(R)^2$ or σ_I(R) are not linear. Since E_a vs. σ_I(R) is linear, $E_a^0 - E_a$ vs. σ_I(R), where E_a^0 is the energy of activation of the first member of the series, is also linear. Replacing E_a^0 and E_a with their equivalents from the Arrhenius equation, we obtain eq 2.

$$\ln (k/k_0) = a\sigma_I(R)/RT + \ln (A/A_0) + b/RT \quad (2)$$

$$E_s' = \ln (A/A_0) + b/RT \quad (3)$$

$$\ln (k/k_0) = a\sigma_I(R)/RT + E_s' \quad (4)$$

$$\log (k/k_0) = \rho^*\sigma^* + \delta E_s \quad (5)$$

By setting the last two terms of eq 2 equal to a constant E_s' (eq 3), we obtain eq 4, which is analogous to Taft's equation (eq 5). Similarly, from the E_a vs. σ_I(R) regression equation we can derive eq 6. If we replace ln k and ln A

$$\ln k = -a\sigma_I(R)/RT + \ln A - b/RT \quad (6)$$

in eq 6 with their equivalents from the respective relations of transition-state theory, we obtain eq 7. Relation 7 is

$$\Delta H^{\ddagger} = a\sigma_I(R) + b \quad (7)$$

$$\Delta H^{\ddagger} = \rho\sigma + \Delta H^{\ddagger}_0 \quad (8)$$

closely analogous to eq 8 which has been shown to hold for systems amenable to Hammett $\rho\sigma$ analysis.[17] Moreover, for the same systems the isokinetic relationship $\delta\Delta H^{\ddagger} = \beta\Delta S^{\ddagger}$ was shown also to hold.[17] Therefore, it seems quite possible that, in systems conforming to the present E_a vs. σ_I(R) analysis, the isokinetic effect may operate.[18]

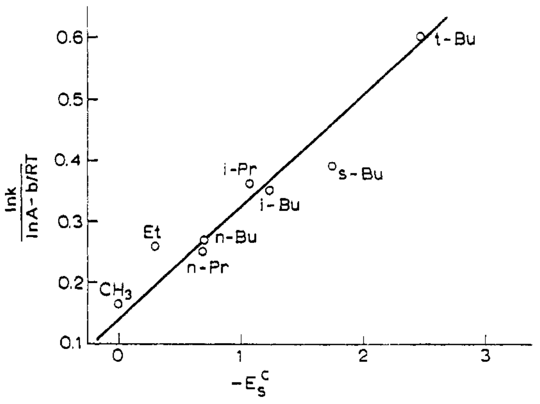

Figure 6. Plot of the inverse of function 9 against E_s^c(R). The ratio was calculated from the regression equation (entry 1, Table I) and from eq 6 at 24.7 °C.

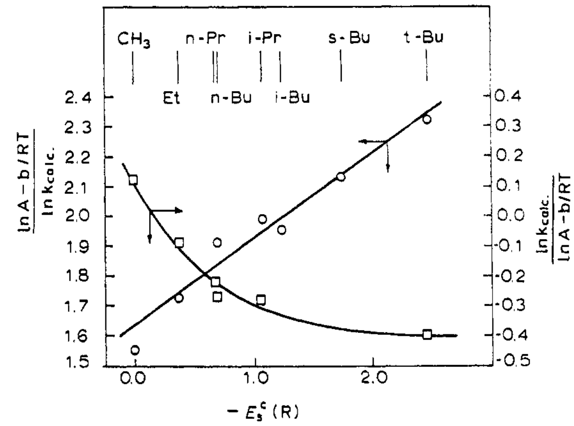

Figure 7. Squares: plot of the inverse of function 9 against E_s^c(R). Circles: similar plot of function 9. Ratios were calculated from eq 6 and from the regression equations of entries 13 and 16 (Table I), respectively, at 25 °C.

Function 3 or the expression ln $A - b/RT$ varies very little with temperature. For example, for the data of Jones and Thomas[2] a 100 K change causes a 25% change in the ratio b/RT (E_a and R in kcal/mol). Neither eq 3 nor the function ln $A - b/RT$ parallels the E_s(R) values or any other steric parameter; rather, they vary as the corresponding ln (A/A_0) or ln A. The data of Jones and Thomas[2] for the alkaline hydrolysis of alkyl acetates indicate that log A's are as follows: *s*-Bu > *n*-Bu > *n*-Pr = *i*-Pr > *i*-Bu > *t*-Bu > Et > CH_3. This order does not correlate either with σ_I(R) or with E_s(R). Only the expressions 9 or 9a seem to be simply related to some steric

$$(\ln A - b/RT)/\ln k_{calcd} \quad (9)$$

$$[\ln (A/A_0) + b/RT]/\ln k_{calcd} \quad (9a)$$

parameter, e.g., E_s^c(R).[19] A plot of the inverse of (9) against E_s^c(R) is nearly linear (Figure 6). Thus it appears reasonable to examine the possibility of using expression 9 to separate the steric effect. The results of this attempt are summarized in Table II. It was noted that depending on the sign of the slope of the E_a vs. $-\sigma_I$(R) regression equation, expression 9 or its inverse could correlate with E_s^c(R) (see Table II). In Figure 7 are given two more

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[16] Reference 15, p 341.

[17] Reference 15, p 376.

[18] Indeed, plots of E_a vs. log A for certain reactions in Table I were nearly linear. This author is indebted to the referees for pointing out the possibility of the involvement of the isokinetic effect.

[19] Hancock, C. K.; Meyers, E. A.; Yager, B. J. *J. Am. Chem. Soc.* **1961**, *83*, 4211.

examples of E_s^c(R) vs. (9) or its inverse plots. One is linear and the other concave. Besides these two types of relationships between expression 9 or its inverse and E_s^c(R), a third type was encountered also, namely, the invariance (entry 13, Table II). It was surprising, and gratifying, that plots of expression 9 vs. E_s^c(R) are linear even for unimolecular gas-phase decomposition reactions (entries 16–18, Table II). It seems possible that a linear relationship between (9) or its inverse and E_s^c(R) means that (9) can separate the steric effect of the substituent provided that the effect has an entropic component dominating over the respective enthalpic one. This follows from the involvement of the Arrhenius preexponential factor in (9). Under the above-mentioned assumption and provided that E_s^c(R) is still a good measure of the steric effect of the substituent for the reactions in entries 4–6 in Table II, the observed curvature in the plot of ln $k_{\text{calcd}}/(\ln A - b/RT)$ vs. E_s^c(R) could mean that the steric effect of the substituent has entropic as well enthalpic components of comparable magnitude. Reactions 13 and 14 (Table II), one of which is the reverse of the other, responded very differently to the present analysis. Only reaction 14, i.e., $R\cdot + CH_4 \rightarrow RH + CH_3\cdot$, showed a variation in the ln $k_{\text{calcd}}/(\ln A - b/RT)$ ratio. Provided again that the above assumptions hold, we are led to the conclusion that steric effects are introduced only by the attacking radical and not at all by the substrate in these ractions. A comment is made now on the physical meaning of expression 9. Perhaps this ratio could be viewed as the fraction of energy assigned to the steric effect of the substituent, whereas the fraction of energy attributed to the inductive effect of the substituent is given by $-a\sigma_I(\text{R})/RT \ln k_{\text{calcd}}$. Notice that the sum of the two ratios is equal to unity.

Let us now examine the correlations between σ_I(R) and steric parameters. If one accepts the view that the σ_I(R scale reflects a combination of hyperconjugation and polarizability effects,[13] then the existing correlation between these constants and steric parameters (entries 9–12, Table I) seems to invalidate the latter ones unless σ_I(R) constants also reflect steric effects. However, derivation of this scale from gas-phase ionization data[14,20,21] seems to preclude this possibility. As an attempt to resolve this confusion, let us consider the various ways of representing a given set of data. The data of Jones and Thomas,[2] for example, have been analyzed (a) by eq 10,[2] (b) by eq 11,[9]

$$\log (k/k_0) = 2.48\sigma^* + E_s \qquad (10)$$

$$\log k = \psi \upsilon_{\text{OX}} + h \qquad (11)$$

and (c) by eq 6. According to eq 10, the change in free energy, $\delta\Delta G^‡$, that is expressed by log (k/k_0) is divided into two parts, both of which depend on the substituent, with an additional constraint that $\rho^* = 2.48$. Analysis by eq 11 requires partition of the free energy expressed by log k into two parts again, but with only one being dependent on the substituent, whereas the other is constant. In spite of this difference in these two alternative representations, the constants E_s and υ_{ox} are linearly related (Figure 8). Given also that the same data are representable by eq 2 or 6 and that υ_{OX} constants are related (entry 9, Table I) to σ_I(R), we are forced to arrive at the following conclusion: a given amount of energy expressed either by E_a or by its analogue, log k, can be divided into two (and perhaps more) parts *arbitrarily*, provided that the partition is done in a consistant manner. Therefore, an apparently successful new representation of kinetic data could not be sufficient evidence against the validity of the parameters used in an alternative representation. For this reason Charton's questioning of the validity of σ^* and σ_I(R) scales[7,11] is unjustified. The validity of the σ_I(R) scale, in particular, is established by the derivation of these constants from gas-phase ionization data[14,20,21] and by its wide utility and applicability to systems markedly different in structure from the defining basis set.[22]

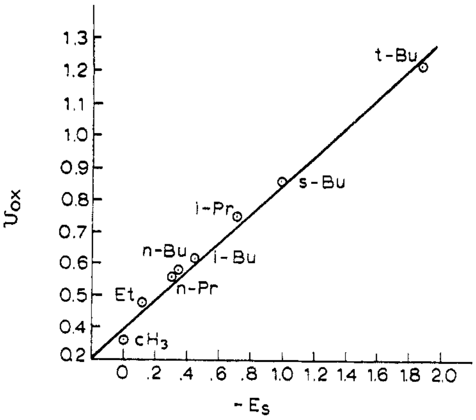

Figure 8. Plot of Charton's υ_{OX} (X = R) against the respective E_s(R) parameters (taken from ref 2).

Conclusions

Kinetic data from reaction series of structurally similar compounds have been represented by a two-kinetic-parameter equation. This analysis, which is applicable to both bimolecular and unimolecular reactions, appears to lead in certain cases to the separation of the steric effect of the substituent. Examination of the various ways of representing a given set of kinetic data revealed that, although the logical bases of the alternative representations were fundamentally different, the substituent constants used were interrelated. For example, Charton's υ_{OX} steric parameters are linearly related to the relevant E_s constants, and also $1/\upsilon_{\text{OX}}$ is linearly related to the respective σ_I(R) constants. This led to the conclusion that a given set of kinetic data can be represented by a number of self-consistent but, nevertheless, arbitrary ways. Therefore, a successful correlation could not be taken as sufficient evidence against the validity of the parameters used in an alternative representation of the same data. For this reason, it is felt that Charton's questioning the validity of the σ^* and σ_I(R) scales is unjustified.

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