Steric Effects on the Formation of Alkyl Radicals and Alkyl Carbenium Ions

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In order to determine the variation of the steric effect with branching on the formation of alkyl radicals and alkyl carbenium ions, logarithms of rate constants for formation were correlated with the branching equation. Significant correlations were obtained for all the sets studied. The results of the correlations are (1) the composition of the alkyl steric effect as a function of branching is highly variable both for alkyl radical and for alkyl carbenium ion formation. No single steric substituent constant could possibly account for all the data. (2) The relative importance of branching at C^2 to that at C^1 is a linear function of the amount of branching in the leaving group. This is true for both alkyl radical and alkyl carbenium ion formation. (3) Whereas branching at C^1 and C^2 causes steric acceleration in the formation of both alkyl radicals and alkyl carbenium ions, branching at C^3 results in steric deceleration. The results demonstrate the utility of the branching equation in the study of the steric effects of alkyl groups. It is capable of representing the complete range of alkyl steric effects, and can detect a change from steric acceleration to steric deceleration due to branching at different carbon atoms of the same alkyl group. The expanded branching equation has been shown to be useful in the determination of the variation of alkyl steric effect with the order of branching at a given carbon atom. Radical formation is much more sensitive to a second branch at C^1 than is carbenium ion formation.

We have shown[1] that rate and equilibrium constants of alkyl substituted systems can be correlated with the extent of branching in the alkyl group by means of the branching

$$Q_X = \sum_{i=0}^{p} a_i n_i \qquad (1)$$

equation (1). In this equation, n_i is the number of C^{i+1} atoms in the alkyl (Ak) group [equation (2)]. Thus, in

$$n_i = \Sigma C^{i+1} \qquad (2)$$

example (1A), in which the alkyl group is bonded to some active site, Y, at which some measurable phenomenon occurs, equations (3)—(7) hold.

$$\Sigma C^1 = n_0 = 1 = \text{constant for all Ak groups} \qquad (3)$$

$$\Sigma C^2 = n_1 = 3 \qquad (4)$$

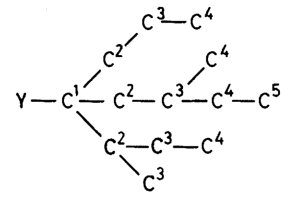
$$\Sigma C^3 = n_2 = 4 \qquad (5)$$

$$\Sigma C^4 = n_3 = 4 \qquad (6)$$

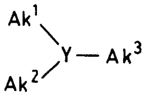
$$\Sigma C^5 = n_4 = 1 \qquad (7)$$

One of the great advantages of the branching equation in the study of steric effects is that, for simple alkyl groups, the number of branches is absolutely free of error. Thus, for the 1-ethylpropyl group, $n_1 = n_2 =$ *exactly* 2. We have extended the method to cycloalkyl groups by calculating effective branching values for C^1, C^2, and when applicable, C^3. These effective n_1, n_2, and n_3 values are, like any ordinary substituent parameter, subject to error. Thus, although we can enlarge the scope of the branching equation by the use of effective n_i values for cycloalkyl groups, we lose the advantage of having error-free parameters. The effective n_i values used here are taken from our earlier work.[2a]

Our previous work showed that the steric effect of alkyl groups varies, and we suggested that it was unlikely that a single steric parameter could account for the behaviour of non-symmetric Ak groups. This conclusion was supported by the results obtained from the correlation of various steric parameters with equation (1). We found[2a] that the dependence of steric parameters (*i.e.* E_S, $E_S{}^o$, $E_S{}^c$, v, and v′) on branching varied widely. Further support for this conclusion comes from the work of Dubois and his co-workers.[2b]



(1A)



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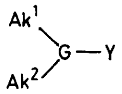
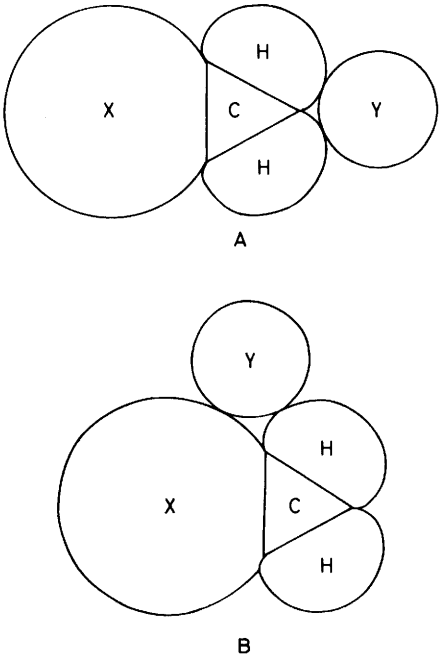


(3)

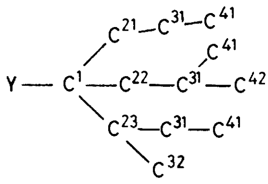
In this work we extend our investigation to the composition, as a function of alkyl branching, of steric effects on the formation of alkyl radicals and alkyl carbenium ions. We are interested in determining the overall effect of branching at C^1—C^3 in an alkyl group. In order to do this, we must extend equation (1) to systems in which there are *j* equivalent Ak groups attached either directly to Y, the active site in (2), or to a skeletal group, G, to which Y is also bonded as in (3). If we assume that the groups are equivalent, the effect of branching is additive and equation (1) becomes (8). The

$$Q_X = \sum_{j=1}^{q} \left(\sum_{i=0}^{p} a_i n_i \right)_j \qquad (8)$$

index *i* refers to the number of the carbon atom in an alkyl group, the index *j* to the number of the alkyl group. Thus, on the solvolysis of $ClCEtPr^iBu$, Y = CCl, Ak^1 = Et, Ak^2 = Pr^i, Ak^3 = Bu, and $\Sigma n_1 = 4$, $\Sigma n_2 = 1$, $\Sigma n_3 = 1$. Note that the carbon atom of the active site Y is excluded in determining n_1—n_3.



Conformations of a CH_2X group interacting with an active site, Y. Top view



(1B)

The simple branching equation, equation (1), assumes that each branch at a carbon atom will exert the same steric effect. This is, of course, only approximately valid. Thus, for many groups of the type CH_2X ($X = F$, Cl, Br, I, H, OH, OMe, Et, SMe, SEt, Ph, CH_2Ph, Me, Et, Pr, NH_2) the value of the steric parameter ν is 0.63 ± 0.065. This value is not very different from that of Me (CH_2X, $X = H$). We have remarked elsewhere that this is an example of the principle of minimal steric interaction. This principle results from the fact that all steric interactions are repulsive and raise the energy of the species in which they occur. It follows, then, that a group whose steric effect is conformationally dependent will prefer that conformation which minimizes steric interactions. Thus, if the CH_2X group is adjacent to the active site, Y, the preferred conformation is A, not B (Figure).

To provide the most accurate, detailed description of the effect of branching, it is necessary to distinguish between the first, second, and third branches at any given carbon atom. Every ith carbon atom in an alkyl group with $i > 1$ must be labelled also by an index by which we may indicate whether it is the first, second, or third branch bonded to the carbon atom $i-1$. Considering the example described above by the simple branching method, we have structure (1B) for the extended branching treatment of (1). As $n_{ib} = \Sigma C(i + 1, b)$ we have equations (9)—(16). Clearly, each n_i in the simple branching equation is replaced by the three variables n_{i1}, n_{i2}, n_{i3}, in the extended branching equation, given by equation (17). The extended branching equation has a major disadvantage in that it may require three times as many independent variables as the simple branching equation. There are few data sets which are sufficiently extensive and well characterized to make effective use of the extending branching equation. Consider, for example, a study of the effect of branching at C^1—C^3 in an Ak group. The extended branching equation could require as many as nine independent variables. To provide two degrees of freedom per independent variable would mean a data set with 30 data points. By contrast, the simple branching equation would require no more than three independent variables and a data set with 12 data points.

$$\Sigma C^1 = n_0 \pm 1 \text{ for all Ak groups}$$

$$\Sigma C^{21} = n_{11} = 1 \tag{9}$$

$$\Sigma C^{22} = n_{12} = 1 \tag{10}$$

$$\Sigma C^{23} = n_{13} = 1 \tag{11}$$

$$\Sigma C^{31} = n_{21} = 3 \tag{12}$$

$$\Sigma C^{32} = n_{22} = 1 \tag{13}$$

$$\Sigma C^{33} = n_{23} = 0 \tag{14}$$

$$\Sigma C^{41} = n_{31} = 1 \tag{15}$$

$$\Sigma C^{42} = n_{32} = 1 \tag{16}$$

$$Q = \sum_{b=1}^{3} \sum_{i=0}^{p} a_{ib} n_{ib} \tag{17}$$

Fortunately, in this work we are interested in comparing the total effect of branching at C^1 with that at C^2 and C^3. For this purpose, the simple branching equation, approximate as it is, provides an adequate description. We have correlated some data sets with the extended branching equation for the purpose of comparison.

In this work we use the extended branching equation (17a) in a form analogous to equation (8).

$$Q = \sum_{j=1}^{q} \left(\sum_{b=1}^{3} \sum_{i=0}^{p} a_{ib} n_{ib} \right)_j \tag{17a}$$

Results and Discussion

Radical Formation.—We have taken rate constants from the literature for radical formation by pyrolysis of hydrocarbons, azo-compounds, and t-butyl peralkanoates and correlated their logarithms with equation (1) or (8), by multiple linear regression analysis. All the data used involve mechanisms which are well established and are discussed in the publications from which the data were taken. Methods of determination and experimental error are also discussed in these original sources. The data used are given in Table 1, the results of the correlations are in Tables 2 and 3. All the data sets studied gave correlations significant at least at the 99.0% confidence level (CL). The results are therefore very good. In order to describe the variation of the steric effect as a function of branching, we now consider the quantity P_i as defined by equation (18) where P_i represents the percentage

$$P_i = \frac{100|a_i|}{\sum_{i=0}^{p} |a_i|} \tag{18}$$

Table 1. Data used in the correlations

(1) k_r, Thermolysis of Ak^{1}Ak^{2}Ak^{3}C–CO$_3$Bu^t in PhEt at60° [a] Y = C–CO$_3$Bu^t

Me, Me, Me, 2.81; Me, Me, Et, 3.64; Me, Me, Pr, 3.49; Me, Me, C$_5$H$_{11}$, 4.41; Me, Me, C$_8$H$_{17}$, 4.85; Me, Et, Et, 6.04; Me, Me, Bu^{t}CH$_2$, 6.47; Et, Et, Et, 8.96; Me, Me, Bu^t, 10.0; Et, Bu, Bu, 11.8; Et, Et, Pr^i, 18.3; Et, Pr^i, Pr^i, 39.4; Pr^i, Pr^i, Pr^i, 70.8

(2) k_r, Thermolysis of *meso*-(AkPhCH)$_2$ in tetralin at 300° [b] Y^1, Y^2 = C–C

Me, 0.098; Et, 0.13; Bu^i, 0.58; CH$_2$Bu^t, 6.8; Pr^i, 0.96; Bu^t, 4.2; Bu^s, 90; t-C$_5$H$_{11}$, 460

(3) k_{rel}, Thermolysis of (*E*)-(Ak^{1}Ak^{2}Ak^{3}C)$_2$N$_2$ in PhEt at 180° [c] Y^1, Y^2 = C–N=N–C

Me, Me, Me, 1.00; Me, Me, Et, 1.19; Me, Et, Et, 1.87; Me, Me, C$_8$H$_{17}$, 2.27; Me, Bu, Bu, 2.60; Me, Me, Pr^i, 3.00; Et, Et, Et, 3.65; Me, Me, Bu^t, 5.30; Me, Et, Pr^i, 5.32; Et, Bu, Bu, 7.26; Me, Me, Bu^t, 7.51; Pr^i, Bu, Bu, 14.4; Me, Et, Bu^t, 16.0; Et, Et, Pr^i, 20.0; Me, Pr^i, Pr^i, 23.0; Me, Et, Bu^t, 36.5; Et, Pr^i, Pr^i, 68.5; Bu^t, Bu, Bu, 107; Bu^t, Et, Et, 107; Pr^i, Pr^i, Pr^i, 206; Me, Me, Bu^{t}CH$_2$, 247; Me, Et, Bu^{t}CH$_2$, 300; Et, Et, Bu^{t}CH$_2$, 365; Me, Pr^i, Bu^{t}CH$_2$, 453

(4) k_{rel}, Thermolysis of AkCO$_3$Bu^t in Bu^{t}CHPr^i at 103.4° [d] Y = CO$_3$Bu^t

cyclo-C$_4$H$_7$, 0.238; cyclo-C$_5$H$_9$, 0.437; cyclo-C$_6$H$_{11}$, 1.02; Pr^i, 1; Me, 0.12; Bu^t, 17.4

(6) k_{rel}, Thermolysis of (*Z*)-(Ak^{1}Ak^{2}Ak^{3}C)$_2$N$_2$ in EtOH at −28.1° [e] Y^1, Y^2 = C–N=N–C

Me, Me, Me, 1.00; Me, Me, Et, 4.4; Me, Me, Pr^i, 64; Me, Me, Bu^i, 153; Me, Et, Et, 37; Et, Et, Et, 1 428

(7) $\Delta G^\ddagger$/kcal mol^{-1}, Thermolysis of (Ak^{1}Ak^{2}CH)$_2$ at 300° [f] Y^1, Y^2 = C–C

Me, Me, 68; Me, cyclo-C$_6$H$_{11}$, 59; cyclo-C$_6$H$_{11}$, cyclo-C$_6$H$_{11}$, 52.1; Bu^t, cyclo-C$_6$H$_{11}$, 42.6; Pr^i, cyclo-C$_6$H$_{11}$, 52.9; Bu^t, Bu^t, 29.6

(8) $\Delta G^\ddagger$/kcal mol^{-1}, Thermolysis of (Ak^{1}Ak^{2}Ak^{3}C)$_2$ at 300° [g] Y^1, Y^2 = C–C

Me, Me, Me, 60.5; Me, Me, Et, 55.3; Me, Me, Pr^i, 46.4; Me, Me, Bu^t, 46.3; Me, Me, cyclo-C$_6$H$_{11}$, 45.8; Et, Et, Et, 43.1; Me, Et, cyclo-C$_6$H$_{11}$, 39.6; Me, Me, Bu^t, 33.7

(9) k_r, Thermolysis of [Ak^{1}Ak^{2}C(CN)]$_2$N$_2$ in PhMe at 80.2° [h] Y^1, Y^2 = C–N=N–C

Me, Me, 1.66; Me, Et, 0.87; Me, Pr, 1.70; Me, Pr^i, 1.03; Me, Bu, 1.58; Me, Bu^i, 7.1; Me, Bu^t, 1.09; Me, CH$_2$Bu^t, 1.36; Me, C$_5$H$_{11}$, 1.63; Pr^i, Pr^i, 1.25; Bu^t, Bu^i, 49.5; Pr^i, Et, 0.95

(10) log k_r, Thermolysis of (*E*)-Ak$_2$N$_2$ at 600° (g) [i] Y^1, Y^2 = –N=N–

Me, −2.62; Et, −1.91; Bu, −1.71; Bu^i, −1.61; Pr^i, −0.90; Bu^s, −0.41; Bu^t, 1.25

(101) k_{rel}, Solvolysis of Ak^{1}Ak^{2}Ak^3–CO–CO–C$_6$H$_4$NO$_2$-4 in 80% v/v aqueous MeAc at 0° [c] Y = CO(CO)C$_6$H$_4$NO$_2$-4

Me, Me, Me, 1.00; Me, Me, Et, 2.13; Me, Et, Et, 3.99; Me, Me, C$_8$H$_{17}$, 2.17; Me, Bu, Bu, 3.96; Me, Me, Pr^i, 2.09; Et, Et, Et, 6.35; Me, Me, Bu^t, 4.50; Me, Et, Pr^i, 5.90; Et, Bu, Bu, 11.1; Me, Me, Bu^i, 4.57; Et, Bu^t, Pr^i, 20.2; Me, Pr^i, Pr^i, 18.4; Me, Et, Bu^t, 48.7; Bu^t, Bu, Bu, 155; Pr^i, Pr^i, Pr^i, 135; Me, Me, Bu^{t}CH$_2$, 13.2

(102) k_r, Solvolysis of Ak^{1}Ak^{2}Ak^{3}CCl in 80% v/v aqueous MeAc at 60° [j] Y = CCl

Me, Me, Me, 1.15; Me, Me, Et, 1.55; Me, Et, Et, 2.17; Me, Me, C$_8$H$_{17}$, 0.89; Me, Me, Pr^i, 1.06; Et, Et, Et, 2.29; Me, Me, Bu^t, 1.63; Et, Bu, Bu, 1.42; Me, Et, Bu^i, 5.74; Me, Et, Bu^t, 5.92; Me, Me, Bu^{t}CH$_2$, 20.1

Table 1 (*continued*)

(103) k_{rel}, Solvolysis of Ak^{1}Ak^{2}Ak^{3}CO–CO–C$_6$H$_4$NO$_2$-4 in 60% v/v aqueous dioxan (0.1M in LiClO$_4$) at 100° [k] Y = CO(CO)-C$_6$H$_4$NO$_2$-4

Me, Me, Me, 1.00; Me, Me, Et, 1.28; Me, Me, C$_8$H$_{17}$, 0.53; Me, Me, Pr^i, 1.93; Me, Me, Bu^i, 3.20; Me, Me, Bu^t, 3.91; Me, Me, CH$_2$Bu^t, 6.40; Me, Et, Et, 2.66; Me, Et, Pr^i, 4.43; Me, Et, Bu^i, 7.75; Me, Et, Bu^t, 17.5; Me, Et, CH$_2$Bu^t, 7.89; Et, Et, Et, 3.84; Et, Et, Pr^i, 9.80; Et, Et, Bu^t, 50; Et, Et, CH$_2$Bu^t, 9.50; Me, Pr^i, Pr^i, 7.10; Et, Pr^i, Pr^i, 18.0; Pr^i, Pr^i, Pr^i, 49.0; Bu, Bu, Et, 0.94; Bu, Bu, Pr^i, 1.34; Bu, Bu, Bu^t, 3.54

(104) k_r, Solvolysis of AkMe$_2$CCl in 80% aqueous EtOH at 25° [l] Y = CCl

Me, 0.0326; Bu^{t}CH$_2$, 0.680; Et, 0.055; Bu, 0.047; Pr, 0.052; Pr^i, 0.029; Bu^t, 0.040

(111), (112) k_r, Solvolysis of AkPhCHCl in 80% aqueous EtOH at 45° and 65°, respectively.[m] Y = CCl

Me, 1 180, 793; Et, 273, 190; Pr, 327, 218; Pr^i, 58.7, 50.0; Bu^t, 2.18, 2.35; t-C$_5$H$_{11}$, 4.58, 4.64; Et$_2$CH, 145, 116

(121), (122), (123) $\delta\Delta H_f$ in (g), (g), SO$_2$ClF respectively [n] Ak^{1}Ak^2-Ak^{3}C$^+$, Y = C$^+$

Me$_3$, 0, 0, 0; Me$_2$Et, −6.1, −8.0, −8.8; Me$_2$Pr, −12.3, −17.6, −15.3; Me$_2$Pr^i, −14.7, −15.9, −15.7; Me$_2$Bu^t, −23.4, −24.6, −18.9; MeEt$_2$, −12.6, −13.8, −15.9; Me$_2$Bu^i, −19.6, −20.4, −20.8

(201) K_e, Dissociation of R^{1}R^{2}R^{3}NBMe$_3$ at 100° (g) [o] Y = NBMe$_3$

H, H, H, 4.6; Me, H, H, 0.0350; Me, Me, H, 0.0214; Me, Me, Me, 0.472; Et, H, H, 0.0705; Et, Et, H, 1.22; Pr, H, H, 0.0598;

Bu, H, H, 0.0470; C$_5$H$_{11}$, H, H, 0.0415; C$_6$H$_{13}$, H, H, 0.0390; Pr^i, H, H, 0.368; Bu^s, H, H, 0.373; Bu^t, H, H, 9.46

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Units of the rate constants in sets 1, 2, 9, 10, 102, 111, 112, are s^{-1}, in set 104, h^{-1}.

of the total steric effect which is due to branching at the *i*th carbon atom. An alternative measure of the dependence of the steric effect of the Ak groups on branching is the quantity φ_{ik}, defined by equation (19). Here φ measures the effect of

$$\varphi_{ik} = a_i/a_k \qquad (19)$$

branching at the *i*th carbon atom relative to the effect at the *k*th carbon atom. In this work, we will set $k = 1$, and consider only φ_{i1} values. Values of P_i, φ_{i1}, and s_φ are given in Table 4.

Table 2. Results of correlations with equations containing three independent variables

Set	X_1	X_2	X_3	X_0	R ^{a}	F ^{b}	r_{12} ^{c}	r_{13} ^{c}
1	0.242	0.0717	0.003 04	0.323	0.9874	116.6	0.405	0.227
3	0.428	0.598	−0.583	−0.374	0.9559	70.57	0.226	0.115
101	0.391	0.303	−0.190	−0.243	0.9574	47.66	0.213	0.120
102	0.145	0.359	−0.481	−0.050	0.9359	16.47 ^{k}	0.153	0.131
103	0.293	0.169	−0.566	−0.164	0.9482	53.49	0.229	0.193
121A	−7.26	−0.659	1.16	22.7	0.9962	130.7 ^{k}	0.707 ^{o}	0.445
122A	−7.96	−0.0835	1.33	23.5	0.9890	44.66 ^{l}	0.707 ^{o}	0.445
123A	−5.81	−0.509	−0.895	16.0	0.9852	32.93 ^{l}	0.707 ^{o}	0.445

Set	r_{23} ^{c}	S_{est} ^{d}	S_2 ^{d}	S_2 ^{d}	S_3 ^{d}	S_0 ^{d}	$100R^2$ ^{e}	ψ ^{f}	n ^{g}
1	0.300	0.0769	0.0135	0.0285 ^{h}	0.0534 ^{l}	0.0475	97.49	0.190	13
3	0.349	0.268	0.0381	0.0505	0.0793	0.139 ^{j}	91.37	0.322	24
101	0.605 ^{j}	0.200	0.0335	0.0645	0.0835 ^{h}	0.111 ^{h}	91.67	0.330	17
102	0.395	0.175	0.0483 ^{h}	0.0559	0.0951 ^{l}	0.149 ^{m}	87.59	0.442	11
103	0.370 ^{o}	0.180	0.0265	0.0376	0.0621	0.0959 ^{n}	89.91	0.351	22
121A	0.026	0.969	0.693 ^{l}	0.680 ^{n}	0.551 ^{p}	2.45 ^{l}	99.24	0.133	7
122A	0.026	1.71	1.22 ^{l}	1.20 ^{l}	0.973 ^{q}	4.32 ^{j}	97.81	0.226	7
123A	0.026	1.72	1.23 ^{l}	1.21 ^{r}	0.977 ^{p}	4.34 ^{h}	97.05	0.262	7

For equation (8), $X_1 = a_1$; $X_2 = a_2$; $X_3 = a_3$; $X_0 = a_0$; for equation (34), $X_1 = a_c$, $X_2 = a_1$, $X_3 = a_2$, $X_0 = a_0$. ^{a} Multiple correlation coefficient. The superscript indicates the confidence level (CL). When no superscript is present, the CL is 99.9%. ^{b} F test. The superscript indicates the CL. When no superscript is present, CL = 99.9%. ^{c} Partial correlation coefficient of the ith independent variable on the jth independent variable. The superscript indicates the CL, in its absence, the CL is <90.0%. ^{d} Standard errors of the estimate, and of the regression coefficients. The superscript indicates the CL of the student t test for the significance of the regression coefficients. In the absence of a superscript, the CL is 99.9%. ^{e} The percent of the variance of the data accounted for by the regression equation. ^{f} The standard error divided by the root mean square of the dependent variable. ^{g} The number of data points in the set. ^{h} 95.0% CL. ^{i} <10.0% CL. ^{j} 98.0% CL. ^{k} 99.5% CL. ^{l} 99.0% CL. ^{m} 30.0% CL. ^{n} 80.0% CL. ^{o} 90.0% CL. ^{p} 50.0% CL. ^{q} 70.0% CL. ^{r} 20.0% CL. ^{s} 60.0% CL. ^{t} 10.0% CL. ^{u} 40.0% CL.

Table 3. Results of correlations with equations containing one or two independent variables

Set	X_1	X_2	X_0	R ^{a}	F ^{b}	r_{12} ^{c}
2	1.13	0.387	−1.69	0.9269 ^{l}	15.25 ^{l}	0.164
4	2.68		−2.18	0.9803	123.4	—
6	1.03	0.685	−0.221	0.9813 ^{l}	39.04	0.234
7	−6.12	2.72	67.9	0.9846 ^{l}	47.47 ^{l}	0.010
8	−7.64	−2.62	61.2	0.9456 ^{l}	21.10 ^{k}	0.241
9	0.003 97	0.497	−0.0362	0.9264	27.22	0.234
10	1.26	0.0221	−2.95	0.9706 ^{l}	32.57 ^{k}	0.155
104	0.108	0.511	−1.86	0.8988 ^{j}	8.412 ^{h}	0.225
111	−0.908	0.305	3.23	0.9796	47.46 ^{k}	0.218
112	−0.832	0.282	3.03	0.9782	44.30 ^{k}	0.218
121B	−7.91	1.21	24.7	0.9947	187.1	0.445
122B	−8.03	1.37	23.7	0.9890	89.18	0.445
123B	−6.29		17.1	0.9770	105.2	
201	−0.426	−0.519	2.23	0.9092 ^{j}	9.635 ^{h}	0.484
211	0.696	0.839	−2.72	0.9278	27.83	0.397

Set	S_{est} ^{d}	S_1 ^{d}	S_2 ^{d}	S_0 ^{d}	$100R^2$ ^{e}	ψ ^{f}	n ^{g}
2	0.580	0.209 ^{l}	0.197 ^{n}	0.455 ^{j}	85.92	0.475	8
4	0.154	0.241		0.202	96.11	0.234	7
6	0.278	0.122 ^{l}	0.157 ^{h}	0.231 ^{p}	96.30	0.278	6
7	3.01	0.631 ^{l}	2.41 ^{s}	2.73	96.94	0.248	6
8	3.24	1.18 ^{l}	1.21 ^{o}	2.60	89.41	0.412	8
9	0.301	0.0807 ^{i}	0.0691	0.186 ^{t}	85.81	0.435	12
10	0.373	0.158 ^{l}	0.196 ^{i}	0.302	94.21	0.318	7
104	0.331	0.146 ^{u}	0.125 ^{j}	0.258 ^{l}	80.79	0.580	7
111	0.248	0.0932	0.132 ^{o}	0.186	95.96	0.266	7
112	0.235	0.0884	0.125 ^{o}	0.177	95.68	0.275	7
121B	1.01	0.432	0.486 ^{o}	2.01	98.94	0.136	7
122B	1.48	0.632	0.711 ^{n}	2.94 ^{l}	97.81	0.196	7
123B	1.61	0.614	—	3.04 ^{l}	95.46	0.252	7
201	0.709	0.187 ^{o}	0.241 ^{o}	0.330 ^{l}	82.66	0.551	7
211	0.327	0.165 ^{l}	0.115	0.314	86.08	0.431	12

For equation (8), $X_1 = a_1$, $X_2 = a_2$, $X_0 = a_0$. For equation (11), $X_1 = S$, $X_0 = h$. R is the simple correlation coefficient. For equation (36), $X_1 = C_0$, $Z_2 = a_1$, $X_0 = a_0$. For equation (3), $X_1 = b_0$, $X_2 = b_1$, $X_0 = b_{10}$. For equation (34), $X_1 = a_c$, $X_2 = a_1$, $X_0 = a_0$. For lettered footnotes, see Table 2.

Table 4. Values of P_c,[g] P_l, φ_{lj}, and S_φ

Set	L.g.[a]	P_c	P_1	P_2	P_3	φ_{21}	S_φ	φ_{31}	S_φ
1	$-CO_3Bu^t$		77.1	22.9		0.296 [b]	0.119		
2	AkPhCH		74.5	25.5		0.342	0.185		
3	(E)-Ak-N=N		26.6	37.2	36.2	1.40 [b]	0.171	−1.36	0.221
4	$-CO_3Bu^t$ [c]		(51.4)	(42.3)	(6.3)	(0.823) [b]			
6	(Z)-AkN=N		60.1	39.9		0.665	0.172		
7	Ak^1Ak^2CH		~100 [d]	~0 [d]		~0 [d]			
8	$Ak^1Ak^2Ak^3C$		74.5	25.5		0.343 [b]	0.167		
9	Z^1-N=N		~0 [e]	~100 [e]		Very large [e]			
101	$Z^2\text{-}\underset{\underset{O}{\|}}{C}O$		44.2	34.3	21.5	0.773 [b]	0.177	−0.485	0.217
102	Cl		14.7	36.4	48.8	2.48 [b]	0.910	−3.32	1.28
103	$Z^2\text{-}\underset{\underset{O}{\|}}{C}O$		28.5	16.4	55.1	0.587 [b]	0.155	−1.93	0.275
104	Cl		0 [e]	100 [e]		Very large [e]			
111	Cl		74.9	25.1		−0.336	0.149		
112	Cl		74.7	25.3		−0.339	0.154		
121		(86.7) [f]		(13.3)					
122		(85.4) [f]		(14.6)					
123		~100							

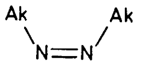
[a] Leaving group. [b] Included in the correlation with equation (31). [c] Values of P_l and φ_{lj} were calculated from a_l obtained for the correlation of ν_{Ak} with the branching equation. [d] These values result because a_2 is not significant. [e] These values result because a_1 is not significant. [f] These values are uncertain since r_{12} shows that n_1 is a linear function of n_c. It is certain, however, that the predominant factor is polarizability and therefore n_c is the significant variable. [g] P_c represents the percent contribution of the variable n_c in correlations with equation (44). $Z^1 = Ak^1Ak^2C(CN)$, $Z^2 = 4\text{-}O_2NC_6H_4$.

Consideration of the values of φ_{21} and P_1 and P_2 clearly shows a wide variation in the composition of the steric effect as a function of branching. The φ_{21} values demonstrate this even more clearly. The standard errors in φ show that the highest and lowest φ_{21} values obtained are significantly different from each other. Then, from the P_l and φ_{21} values, it is certain that no single steric parameter can possibly represent the steric effect of Ak groups in radical formation.

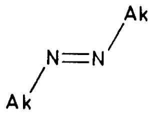
For the purpose of clarifying our later discussion, at this point it is useful to note that we assume all steric effects are due to electronic repulsion between orbitals on atoms which are not directly bonded to each other. If repulsion is greater in the reactant than in the transition state (rate) or product (equilibrium) the result is steric augmentation; if the reverse is the case, the result is steric diminution. It has been pointed out that the use of the terms steric acceleration and deceleration should properly be restricted to rates. We needed terms which are generally applicable and which define any increase in a measurable quantity, Q, which results from the steric effect of some group as steric augmentation. Any decrease is then steric diminution. We shall use these expressions for all types of quantitative data, whether chemical reactivities or physical properties.

We now consider the sign of a_l. A positive a_l indicates steric augmentation and a negative a_l diminution. Our results for radical formation show that in all cases the a_1 and a_2 values are positive. The effect of branching at C^1 and C^2, then, is steric augmentation. This is presumably due to relief of steric strain in the transition state for radical formation. In the only set of data for which the effect of branching at C^3 can be effectively studied (set 3) we observe that the a_3 value is negative, indicating steric diminution. We shall discuss this observation later.

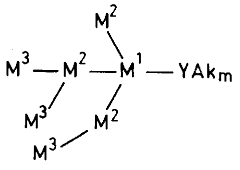
We may also note on comparing the φ_{21} values that pyrolysis of the Z-configuration dialkylazo-compounds (4) is more sensitive to branching at C^2 than for the E-configuration. We can attribute this to a repulsion between branches at C^2 in the alkyl groups of the Z-configuration which cannot occur in the E-configuration.



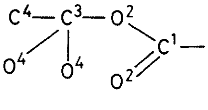
(4*Z*)



(4*E*)



(5A)



(5B)

We may make one additional observation regarding the steric effect on alkyl radical formation. The φ_{21} values increase as the degree of branching at M^1 and M^2, the first and second atoms of the leaving group, increases. A leaving group written in this form is shown in (5A) where the M^l are the atoms of which the leaving group is composed. As an example, consider the leaving group of set 1 (5B). In (5B), M^2 is oxygen and M^1, M^3, and M^4 are carbon.

We may now consider the treatment of a set of data for rates of pyrolysis of $AkCO_3Bu^t$ (set 4, Table 1) which cannot be treated at the present time by correlation with equation (1). The inapplicability of equation (1) results from the fact that several of the data points are for cycloalkyl groups (cAk). Branches which are part of a cAk group do not behave sterically in the same way as acyclic branches. They can be treated by the branching equation only if 'effective' branching constants have been evaluated for them.[2] We have therefore examined the correlation of the data with the modified

Taft equation (20) where υ is a steric parameter defined from the van der Waals radii of X and H by equation (21). Correlation was successful and the statistics obtained are presented in Table 3. Since we have shown elsewhere that equation (22)

$$Q_X = S\upsilon_X + h \tag{20}$$

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \tag{21}$$

$$\upsilon_X = \Sigma a_i^0 n_i \tag{22}$$

holds we may use the values of $a^0{}_i$ to calculate a_i for the correlation of log K with the branching equation by simply substituting equation (22) in (20) and equating this to equation (1) giving (23). Values of P_i and φ_i were calculated from the a_i values obtained from equation (23). They are given in Table 4.

$$a_i = S a_i^0 \tag{23}$$

Another problem of interest is the correlation of rates for the pyrolysis of (*E*)-dialkylazo-compounds, (set 9, Table 1) in which Ak = $R^1R^2R^3C$ with R = H or alkyl. In this case we are varying not only steric effects but electrical effects as well. This results from the fact that although the electrical effects of Ak groups are constant [3,4] some authors still believe that alkyl groups exert variable electrical effects depending on the degree of branching. We know of no unequivocal evidence in favour of this viewpoint and have amassed a considerable body of evidence against it. Until and unless clearcut, unambiguous evidence of the variability of alkyl electrical effects is presented, we shall consider these effects to be constant.

$$\sigma_{I,Ak} = -0.01 \pm 0.02 = 0 \tag{24}$$

$$\sigma_{D,Ak} = \text{constant} \neq 0 \tag{25}$$

The number of alkyl substituents bonded to the incipient radical carbon varies from 0 to 3.

We may express the effect of R^1—R^3 on the formation of $Ak^{\cdot}$ by equation (6) which assumes additivity of substituent effects. Thus, we have equation (26). For R = H, $\sigma_I \equiv \sigma_D \equiv \upsilon \equiv 0$. From equations (8), (22), and (23), we have equation (27). Now equations (28) and (29) hold where $n_{Ak'}$ is the number of alkyl groups in Ak. Then, we have equation (30). As equations (31) and (32) apply we obtain (33). If we need to consider branching only at C^0 and C^1 ($i \leq 1$) then we have equations (34) and (35). The correlation equation actually used was (36).

$$\log K_{Ak} = L\Sigma\sigma_{IR} + D\Sigma\sigma_{DR} + D\Sigma\upsilon_R + h \tag{26}$$

$$\log K_{Ak} = L\Sigma\sigma_{IR} + D\Sigma\sigma_{DR} + \sum_{j=1}^{q}\left(\sum_{i=0}^{p} a_i n_i\right)_j \tag{27}$$

$$\Sigma\sigma_{IR} = n_{Ak'}\sigma_{I,Ak'} \tag{28}$$

$$\Sigma\sigma_{DR} = n_{Ak'}\sigma_{D,Ak'} \tag{29}$$

$$\log k_r = n_{Ak}\,(L\sigma_{ISAk'} + D\sigma_{DSAk'}) + \sum_{j=1}^{q}\left(\sum_{i=0}^{p} a_i n_i\right)_j \tag{30}$$

$$\Sigma C(1) = n_0 = n_{Ak'} \tag{31}$$

$$L\sigma_{ISAk'} + D\sigma_{DSAk'} = b_0 \tag{32}$$

$$\log k_r = b_0 n_0 + \sum_{j=1}^{q}\left(\sum_{i=0}^{p} a_i n_i\right)_j \tag{33}$$

$$\log k_r = b_0 n_0 + a_0 n_0 + a_1 n_1 \tag{34}$$

$$= c_0 n_0 + a_1 n_1 \tag{35}$$

$$\log k_r = c_0 n_0 + a_1 n_1 + a_{10} \tag{36}$$

Carbenium Ion Formation.—We now turn our attention to steric effects upon the formation of alkyl carbenium ions. Again, the data studied are set forth in Table 1 and results of the correlation in Tables 2 and 3. Values of P_i and φ_{i1} are in Table 4. The correlations are, except for set 104, highly significant. The values of P_1 and P_2 again indicate the impossibility of representing the alkyl steric effect by a single steric substituent parameter. Further support is obtained by a consideration of φ_{21} and S_φ values. It follows then that the steric effects of alkyl groups on the formation of alkyl carbenium ions cannot be represented by a single set of steric parameters, in agreement with our results for alkyl radical formation.

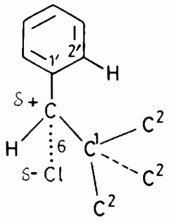
The signs of a_1 and a_2 are positive and therefore the effect of branching at C^1 and C^2 is steric augmentation, presumably as a result of the relief of steric strain in the reactant. In the two sets for which the effect of branching at C^3 can be determined, a_3 is negative and steric diminution occurs. It will be recalled that this was also the case in the only set of radical formation rates for which a_3 could be determined. Thus, in the case of both alkyl radical and alkyl carbenium ion formation, branching at C^3 increases steric repulsion in the transition state relative to the reactant.

This is readily understood if we consider that relief of steric strain due to a change in hybridization from sp^3 in the reactant to something approaching sp^2 in the transition state will decrease as we go down the chain of an alkyl group. Thus, the greatest relief of steric strain should be at C^1. There should be much less at C^2 and very much less at C^3. Then, it is quite reasonable that other steric effects predominate over the relief of steric strain in branching at C^3, and that the overall effect is steric diminution.

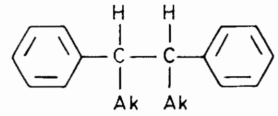
The results obtained for solvolysis of AkCHPhCl also show a difference in the sign of a_i, thus a_2 is positive and a_1 is negative. By contrast, in the pyrolysis of $(PhAkCH)_2$ we find that both a_1 and a_2 are positive. We can account for this strikingly different behaviour in the following manner. (a) The Cl leaving group in the solvolysis of AkPhCHCl (6) is very much smaller than the AkPhCH 'leaving group' in the pyrolysis of $(AkPhCH)_2$ (7). Thus, branching at C^1 exerts a larger effect in the latter than in the former. (b) The transition state for the solvolysis of G is likely to be close to the carbenium ion (8). Then, C^1 of the Ak group, the Ph group, and the incipient carbenium ion carbon should all be approximately coplanar. Inspection of (8) suggests the possibility of considerable steric repulsion between one of the *ortho*-hydrogen atoms in the Ph group and branches on C^1. This is the major contribution to the effect of branching at C^1 due to the small size of the leaving group.

We again observe that, for the formation of $Ak^1Ak^2Ak^3C^+$ carbenium ions, the effect of branching at C^2 increases with the increasing size of the leaving group.

The Effect of the Leaving Group.—It seemed of interest to attempt to quantify the effect of the leaving group on the steric effect due to branching at C^1 and C^2. We begin by recognizing that if for any particular data set, a steric parameter of the correct composition is available, υ_c, then the



(8)



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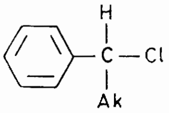

(6)

modified Taft equation applies, and we have equation (37).

$$Q_{\mathrm{Ak}} = S\,\upsilon_{\mathrm{c,Ak}} + h \qquad (37)$$

In this equation, the steric substituent parameter, υ_c, represents the steric effect, and the steric reaction parameter, S, represents the effect of reaction conditions such as medium, temperature, pressure, and reagent. As any steric parameter can be represented as a function of branching, equation (38) results. Thus, from equations (23) and (18), we have (39) and from (23) and (19), (40). It follows, then, that P_i and φ_{ik} are

$$\upsilon_c = \Sigma a_i^0 n_i \qquad (38)$$

$$P_i = \frac{100S|a_i^0|}{S\Sigma|a_i^0|} = \frac{100|a_i^0|}{\Sigma|a_i^0|} \qquad (39)$$

$$\varphi_{ik} = \frac{Sa_i^0 m}{Sa_k^0} = \frac{a_i^0}{a_k^0} \qquad (40)$$

dependent only on the steric effect composition, and are independent of the reaction conditions.

We now consider the correlation of φ_{21} values for seven of the sets studied with the branching equation. The variables are the extent of branching at the atoms M^1 and M^2 in the leaving group. Thus, the correlation equation is (41). The

$$\varphi_{21} = b_0 n_0 + b_1 n_1 + b_{10} \qquad (41)$$

φ_{21} values included in the correlation are those for the formation of $Ak_3C^\bullet$ and Ak_3C^+; they are noted in Table 4. As in this set any bond from an M^1 or M^2 atom to some atom other than a hydrogen counts as a branch, equation (41) is only a crude model. We have noted elsewhere that the branching effect depends on the type of branching atom.[5] Nevertheless, correlation with equation (41) is significant (for statistics, see set 201, Table 3) and the results show that the major factor determining steric effect composition in alkyl radical and carbenium ion formation is the degree of branching at the first atom [M^1] of the leaving group.

ΔH_f *for Carbenium Ions.*—Finally, we turn our attention to the enthalpies of formation of alkyl carbenium ions in the gas phase, and in SO_2ClF. Reports have appeared which show that gas phase reactions can exhibit a significant dependence on polarizability.[3c,6] A useful measure of polarizability is the group molar refractivity.[7] We have defined the polarizability parameter α by equation (42) where MR_X and MR_H are the

$$\alpha = (MR_X - MR_H)/100 \qquad (42)$$

molar refractivities of X and H, respectively.[2] We have also shown that for alkyl groups, equation (43) in which n_c is the

$$MR_{\mathrm{Ak}} = a_c n_c + a_0 \qquad (43)$$

number of carbon atoms in the alkyl group, is obeyed. As in the data available (sets 121—123) only branching at C^1 and C^2 need be considered, we have correlated the data with equation (44).

$$Q_X = a_c n_c + a_1 n_1 + a_2 n_2 + a_0 \qquad (44)$$

Significant correlations were obtained (sets labelled A, in Table 2) and the best results arose by excluding n_1 (sets labelled B in Table 3). The results show that the major factor in the variation of ΔH_f with structure in both the gas phase and in SO_2ClF is the polarizability. There seems to be a barely significant dependence on branching at C^2 in the gas phase data. No dependence on branching, and therefore no steric effect, can be detected in the SO_2ClF data. Due to the small data sets available, the conclusions regarding the steric effect on ΔH_f can only be regarded as tentative. That the major effect is due to polarizability seems fairly certain.

Borane–Alkylamine Adducts and Leaving Group Steric Effects.—Some corroboration of our results on the effect of leaving group branching can be obtained by a consideration of the data obtained by Brown[8] and his co-workers for the dissociation of $R^1R^2R^3NBMe_3$[9] (R = Ak or H) in the gas phase. This reaction is formally analogous to the formation

$$R^1R^2R^3NMBe_3 \underset{}{\overset{K_e}{\rightleftharpoons}} R^1R^2R^3N + BMe_3$$

of a carbenium ion with $R^1R^2R^3N$ as the leaving group. The discussion regarding the correlation of rates of thermolysis of (*E*)-Ak_2N_2 (set 10) is applicable here as well. Since this process is taking place in the gas phase, we must also take into account the possible importance of polarizability as discussed above with regard to the correlation of the enthalpies of formation of carbenium ions in the gas phase. We have therefore made use of equation (45). As a_c and a_2 were not

$$Q_{R^1R^2R^3} = a_c\Sigma n_c + a_0\Sigma n_0 + a_1\Sigma n_1 + a_2\Sigma n_2 a_{10} \qquad (45)$$

significant, we correlated the data with equation (36) obtaining significant results (set 211, Table 3). The data used in the correlation are set forth in Table 1. While Σn_0 is a function of both electrical and steric effects, n_1 is a measure only of the steric effect of branching at C^1. The significance of n_1 as a parameter supports the argument that branching in a leaving group can have an important effect on reactivity.

Correlation with the Extended Branching Equation.—We have correlated sets 3 and 103 with the extended branching equation [equation (7)]. The results are set forth in Table 5. The correlation equation used was (46). In the sets studied,

$$Q = a_{11}\Sigma n_{11} + a_{12}\Sigma n_{12} + a_{13}\Sigma n_{13} + a_{21}\Sigma n_{21} + a_{22}\Sigma n_{22} + a_{23}\Sigma n_{23} + a_0 \qquad (46)$$

$\Sigma n_{32} = \Sigma n_{33} = 0$ and Σn_{31} is highly linear in Σn_{21}. We can therefore consider the effect of branching as a function of b [the index which indicates whether a branch is the first,

Table 5. Results of correlations with the extended branching equation

Set	a_{11}	a_{12}	a_{13}	a_{21}	a_{22}	a_{23}	a_0	R^{a}
3	0.307	0.455	0.549	0.0627	0.713	1.21	−0.196	0.9785
103	0.292	0.221	0.445	−0.409	0.808	0.0505	−0.139	0.9722
Set	F^{b}	r_{1112}^{c}	r_{1113}^{c}	r_{1121}^{c}	r_{1122}^{c}	r_{1123}^{c}	r_{1213}^{c}	r_{1221}^{c}
3	63.85	0.277	0.092	0.255	0.111	0.000	0.489^{h}	0.348
103	43.05	0.283	0.093	0.279	0.120	0.000	0.498^{h}	0.323
Set	r_{1222}^{c}	r_{1223}^{c}	r_{1321}^{c}	r_{1322}^{c}	r_{1323}^{c}	r_{2122}^{c}	r_{2123}^{c}	r_{2223}^{c}
3	0.380	0.241	0.186	0.277	0.215	0.287	0.223	0.775^{v}
103	0.486^{h}	0.356	0.149	0.275	0.201	0.342	0.250	0.733^{v}
Set	S_{est}^{d}	S_{11}^{d}	S_{12}^{d}	S_{13}^{d}	S_{21}^{d}	S_{22}^{d}	S_{23}^{d}	
3	0.204	0.0550	0.0792	0.0925	0.0653^{s}	0.163	0.179	
103	0.146	0.0400	0.0605	0.0670	0.0515	0.120	0.135^{r}	

Set	S_0	$100R_2^{e}$	n^{g}
3	0.115^{n}	95.75	24
103	0.0838^{n}	94.51	22

For footnotes *a—u*, see Table 2. ^{v} 99.9% CL.

second, or third at a given C^i] only at C^1. Applying equation (19) we can calculate φ'_{i1} values from equation (47).

$$\varphi'_{i1} = a_{ib}/a_{i1} \qquad (47)$$

For set 3, we have $\varphi'_{12} = 1.48 \pm 0.37$, $\varphi'_{13} = 1.79 \pm 0.44$; for set 103, $\varphi'_{12} = 0.76 \pm 0.22$, $\varphi'_{13} = 1.52 \pm 0.31$. Both sets give φ_{13} values which are not significantly different from each other. The φ_{12} values are significantly different, however. Radical formation is more strongly affected by the second branch at C^1 than by the first. For carbenium ion formation, the reverse is observed.

The linearity of Σn_{31} with Σn_{21} and of Σn_{23} with Σn_{22} makes it impossible to resolve the dependence of branching on *b* at C^2 in these data sets. Furthermore, no conclusion on the variation of the steric effect with branching at C^i can be reached due to collinearity. By contrast, the results with the simple branching equation are unaffected by collinearity, making it possible to reach conclusions on the variation of the steric effect with branching at C^i. The extended branching equation has allowed the variation of the steric effect at C^1 with *b* to be studied, however. It seems reasonable to make use of both the simple and extended branching equations whenever possible. They both contribute to an understanding of the variation of Ak steric effects with branching.

Conclusions.—We may summarize our results as follows. (1) In the formation of alkyl radicals and alkyl carbenium ions, the variation in the composition of the steric effect as a function of branching is very large. No single steric substituent constant can possibly account for all the observed steric effects. (2) The most important factor in determining the relative importance of branching at C^2 to that at C^1 is the degree of branching at the first atom of the leaving group. This is true for both alkyl radicals and alkyl carbenium ion formation. (3) Branching at C^1 and C^2 causes steric augmentation in both alkyl radical and alkyl carbenium ion formation, branching at C^3 apparently results in steric diminution. Thus, different portions of the same alkyl group can have opposite steric effects on the reactivity. (4) The expanded branching equation was developed to represent the variation of alkyl steric effect with the order of branching at a given carbon atom. It has been applied with some success to two data sets. Radical formation is much more sensitive to a second branch at C^1 than is carbenium ion formation. (5) The branching equation is a very useful method for the study of steric effects of alkyl groups. It accommodates the entire range of steric effect composition and permits the detection of opposing steric effects in different parts of the same alkyl group.

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