Steric Effects. I. Esterification and Acid-Catalyzed Hydrolysis of Esters

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Abstract: Rate constants for the esterification of six sets of XCO_2H were correlated with v values defined from $v_X = r_{VX} - r_{VH} = r_{VX} - 1.20$, where r_{VX} and r_{VH} are the van der Waals radii of the X group and the hydrogen atom, respectively. The correlation equation was the modified Taft equation, $\log k_X = \psi v_X + h$. The very good results obtained indicate that the rates of acid-catalyzed esterification are solely a function of steric effects. New v values were then calculated for many groups from these correlations. The v values were used to correlate rate constants for 22 sets of esterification and acid-catalyzed ester hydrolysis and alcoholysis with the modified Taft equation with generally excellent results. The relationship $v_{CX_nH_{3-n}} = m v_{CMe_nH_{3-n}} + c$ was shown to hold. From this equation, additional v values could be estimated. A total of 61 v values are reported. The use by Taft of average values of $\log (k_X/k_{Me})_A$ in the determination of E_s constants was shown to be invalid. It was also shown that the corrected steric parameters of Hancock (E_s^c) and of Palm (E_s^o) cannot in fact contain a correction for hyperconjugation and furthermore are unnecessary.

Steric effects were first treated quantitatively by Taft,[1] who proposed the equation

$$\log (k/k_0) = \delta E_{sX} \qquad (1)$$

where E_s is a parameter characteristic of the X group. We have shown previously[2] that the Taft E_s values are linear in van der Waals radii and are therefore true measures of the steric effect. The E_s values were defined from the equation

$$E_s \equiv \log (k/k_0)_A \qquad (2)$$

where k and k_0 are the rate constants for acid hydrolysis of the substituted ester and the ester bearing a methyl group in the acyl moiety. For substituents conjugated with the carbonyl group of the ester, E_s is believed to include resonance effects. The purposes of this investigation are threefold. First, in defining E_s values, Taft used average values of $\log (k/k_0)_A$ obtained from: (1) hydrolysis of ethyl esters in 70% v/v aqueous acetone at 25°; (2) esterification of carboxylic acids in MeOH at 25°; (3) esterification of carboxylic acids with EtOH at 25°; (4) hydrolysis of ethyl esters in 60% v/v aqueous acetone at 25°. This is based on the assumption that δ in eq 1 is the same for all of the above defining reactions. We have investigated this assumption.

In the second place, we wished to investigate the validity of the hyperconjugation corrections introduced by Hancock[3,4] and by Palm.[4,5] Thus, Hancock and his coworkers proposed the equation

$$E_s = E_s^c + (-0.306)(n - 3) \qquad (3)$$

where n is the number of α-hydrogen atoms in the substituent. Palm proposed to account for both C–C and C–H hyperconjugation by means of the equation

$$E_s = E_s^o - 0.33(n_H - 3) - 0.13n_C \qquad (4)$$

where n_H is the number of α-hydrogen atoms and n_C the number of α-carbon atoms.

Finally, in the next paper of this series, we hope to examine the Taft separation of polar and steric effects. For this purpose, it is necessary to correlate rate data for the acid hydrolysis of esters with reliable steric parameters.

In order to achieve the above objectives, we have defined new steric-effect substituent constants based on van der Waals radii. In other work,[6] we have defined the steric parameter v by means of the relationship

$$v_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \qquad (5)$$

where r_{VX} is the van der Waals radius of the X group, and

r_{VH} is the van der Waals radius of the hydrogen atom. For tetrahedral substituents such as methyl and *tert*-butyl, the calculated values of $r_{V,min}$ were used.[2] Rates of esterification of substituted carboxylic acids with methanol or ethanol were correlated with the v constants by means of the equation

$$\log k = \psi v + h \qquad (6)$$

Only those substituents for which v constants were available were included in the correlation. The sets studied (1–6) are given in Table I; the results of the correlations are in Table II. The constants used in the correlation are given in Table III. The results obtained for these sets are remarkably impressive, although the sets are of minimal size. The substituents studied show a range of v from 0 to 1.56. It seems reasonably certain that the rates of acid-catalyzed esterification are therefore dependent on steric effects alone at least for the substituents studied. Resonance effects of the substituents studied as measured by the σ_R constants show no dependence on v values. This is also true of localized (field and/or inductive) effects as measured by the σ_I constants.

It is not possible at the present time to calculate v values for substituents other than those of the type A_3B (such as CH_3, CMe_3, CCl_3, etc.) or single atom substituents such as F, Cl, H. We have therefore used the successful correlations obtained in sets 1–6 to estimate new v values for a number of substituents. The values of v obtained in this manner are set forth in Table III.

By means of these v values we have correlated with eq 6 22 sets of esterification, acid-catalyzed hydrolysis of esters, and acid-catalyzed alcoholysis of esters. The data used in these correlations are set forth in Table I. Results of the correlations are set forth in Table II. Of the 22 sets studied, 19 gave excellent results. The remaining 3 sets gave poor but significant results. These sets had only three points however; undoubtedly had more data been available, these sets would also have given excellent results. It must be noted that the value of v obtained from sets 4, 5, and 6 for Et_2CH did not give good results with sets 7, 8, and 9. A new value of v for this group was defined from these sets. Again the values of v for Ph from ref 2 and $CHCl_2$ from set 2 did not give good results with set 21. A new value of v for Ph was calculated from sets 4, 5, and 6 and used with set 21. A new value of v for $CHCl_2$ was then calculated from that set. The question then arises as to which v value is to be preferred when two different values are obtained. We have answered this question in the following manner. We have ob-

Table I. Data Used in Correlations

1	k, XCO_2H + MeOH in MeOH at 15°, catalyzed by HCl[a] H, 1124; Me, 104; Cl_3C, 0.969	14	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O v/v at 50°, catalyzed by HCl[f] Pr, 15.9; $BuCH_2$, 15.1; $Bu(CH_2)_4$, 11.8; i-Pr, 11.7; s-$BuCH_2$, 3.55; $Ph(CH_2)_3$, 11.2; i-$PrCH_2CH_2$, 14.5; c-C_6H_{11}, 6.20; $PhCH_2$, 12.0; $Ph(CH_2)_2$, 11.0; $Ph(CH_2)_4$, 12.1; PhMeCH, 0.251; PhEtCH, 0.103; Ph_2CH, 0.0506; c-$C_6H_{11}CH_2$, 4.41
2	k, XCO_2H + EtOH in EtOH at 14.5°, catalyzed by HCl[b] Me, 3.661; t-Bu, 0.0909; CCl_3, 0.03712; CBr_3, 0.01345		
3	$10^4 k$, XCO_2H + EtOH in EtOH at 25°;[c] Me, 148; t-Bu, 2.19; CCl_3, 1.14	15	$10^2 k$, XCO_2H + MeOH in MeOH at 50°, catalyzed by HCl[d] Me, 21.9; Et, 19.3; Pr, 10.3; Bu, 10.1; $BuCH_2$, 10.2; $Bu(CH_2)_4$, 10.0; i-Pr, 7.27; i-Bu, 2.48; s-Bu, 2.19; i-$PrCH_2CH_2$, 10.4; $PhCH_2$, 9.44; $PhCH_2CH_2$, 9.20; $Ph(CH_2)_3$, 10.0; s-$BuCH_2$, 2.40; t-Bu, 0.858; Et_2CH, 0.253; Pr_2CH, 0.227; Bu_2CH, 0.207; $(i$-Bu$)_2CH$, 0.105; c-$C_6H_{11}CH_2$, 2.79; c-$C_6H_{11}CH_2CH_2$, 10.6; c-$C_6H_{11}(CH_2)_3$, 9.41; PhEtCH, 1.05; Ph_2CH, 0.778; $Ph(CH_2)_4$, 10.2; c-C_6H_{11}, 4.38
4	$10^3 k$, XCO_2H + MeOH in MeOH at 20°, catalyzed by HCl[d] H, 632; Me, 44.0; t-Bu, 1.40		
5	$10^3 k$, XCO_2H + MeOH in MeOH at 30°, catalyzed by HCl[d] H, 1110; Me, 81.4; t-Bu, 2.68		
6	$10^3 k$, XCO_2H + MeOH in MeOH at 40°, catalyzed by HCl[d] H, 1730; Me, 132; t-Bu, 4.93		
7	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O at 24.8°, catalyzed by HCl[e] Me, 4.47; Et, 3.70; Pr, 1.96; Bu, 1.79; $BuCH_2$, 1.77; i-Pr, 1.46; i-Bu, 0.572; t-Bu, 0.128; $PhCH_2$, 1.58	16	$10^2 k$, XCO_2H + MeOH in MeOH at 25°, catalyzed by HCl[g] Me, 5.93; Et, 5.73; i-Pr, 1.95; $PhCH_2$, 2.62; t-Bu, 0.194; Ph_2CH, 0.185
8	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O at 35.0°, catalyzed by HCl[e] Me, 10.9; Et, 9.24; Pr, 4.83; Bu, 4.45; $BuCH_2$, 4.30; i-Pr, 3.43; i-Bu, 1.46; t-Bu, 0.363; $PhCH_2$, 3.84	17	$10^6 k$, XCO_2Et + H_2O in 60% EtOH–H_2O v/v at 24.86°[h] Me, 43.8; $ClCH_2$, 39.48; Cl_2CH, 21.26; CCl_3,[i] 82.6
9	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O at 44.7°, catalyzed by HCl[e] Me, 24.7; Et, 20.7; Pr, 10.8; Bu, 10.2; $BuCH_2$, 9.76; i-Pr, 7.46; i-Bu, 3.30; t-Bu, 1.10; $PhCH_2$, 8.84	18	$10^6 k$, XCO_2Et + H_2O in 60% EtOH–H_2O v/v at 39.79°[h] Me, 161.4; $ClCH_2$, 134.8; Cl_2CH, 65.9; CCl_3,[i] 238.6
10	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O v/v at 20°, catalyzed by HCl[f] Pr, 1.14; $BuCH_2$, 1.10; $Bu(CH_2)_4$, 0.868; i-Pr, 0.865; s-$BuCH_2$, 0.250; i-$PrCH_2CH_2$, 1.04; c-C_6H_{11}, 0.473; $PhCH_2$, 0.934; $PhCH_2CH_2$, 0.805; $Ph(CH_2)_3$, 0.800; $Ph(CH_2)_4$, 0.861; PhCHMe, 0.0171; PhCHEt, 0.00669; Ph_2CH, 0.00296; c-$C_6H_{11}CH_2$, 0.300	19	$10^6 k$, XCO_2Et + H_2O in 60% EtOH–H_2O v/v at 60.04°[h] Me, 785; $ClCH_2$, 619; Cl_2CH, 270.4; CCl_3,[i] 761; Ph, 3.92
		20	$10^6 k$, XCO_2Et + H_2O in 60% EtOH–H_2O v/v at 80.10°[h] Me, 3163; $ClCH_2$, 2259; Cl_2CH, 925; CCl_3,[i] 2166; Ph, 20.5
11	$10^5 k$, EtO_2CX–H_2O in 70% MeAc–H_2O v/v at 25°, catalyzed by HCl[f] $PhCH_2$, 1.47; $PhCH_2CH_2$, 1.28; $Ph(CH_2)_3$, 1.27; $Ph(CH_2)_4$, 1.39; PhMeCH, 0.277; PhEtCH, 0.110; Ph_2CH, 0.0503; c-$C_6H_{11}CH_2$, 0.481; Me, 4.55; Et, 3.77; Pr, 1.86; Bu, 1.82	21	$10^7 k$, XCO_2Et + H_2O in 60% MeAc–H_2O v/v at 25°, catalyzed by HCl[j] Ph, 1.29; i-Pr, 210; $ClCH_2$, 382; H, 10, 700
		22	$10^3 k$, XCO_2-2-$C_{10}H_8$ + MeOH in MeOH at 25°, catalyzed by HCl[k] Me, 378; Et, 238; Pr, 140; $BuCH_2$, 116; i-Pr, 54.9; t-Bu, 2.71
12	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O v/v at 30°, catalyzed by HCl[f] Pr, 2.99; $BuCH_2$, 2.81; $Bu(CH_2)_4$, 2.20; i-Pr, 2.07; s-$BuCH_2$, 0.646; i-$PrCH_2CH_2$, 2.68; c-C_6H_{11}, 1.15; $PhCH_2$, 2.37; $PhCH_2CH_2$, 2.05; $Ph(CH_2)_3$, 2.04; $Ph(CH_2)_4$, 2.24; PhMeCH, 0.0447; PhCHEt, 0.0178; Ph_2CH, 0.00836; c-$C_6H_{11}CH_2$, 0.780	23	$10^3 k$, XCO_2-2-$C_{10}H_8$ + EtOH in EtOH at 25°, catalyzed by HCl[k] Me, 91.2; Et, 50.7; i-Pr, 8.58
		24	$10^3 k$, XCO_2-2-$C_{10}H_8$ + PrOH in PrOH at 25°, catalyzed by HCl[k] Me, 87.6; Et, 45.8; Pr, 24.0; $BuCH_2$, 23.3; i-Pr, 7.30; t-Bu, 0.210
13	$10^5 k$, EtO_2CX + H_2O in 70% MeAc–H_2O v/v at 40°, catalyzed by HCl[f] Pr, 6.92; $BuCH_2$, 6.72; $Bu(CH_2)_4$, 5.19; i-Pr, 5.03; s-$BuCH_2$, 1.52; i-$PrCH_2CH_2$, 6.16; c-C_6H_{11}, 2.62; $PhCH_2$, 5.49; $PhCH_2CH_2$, 4.76; $Ph(CH_2)_3$, 4.86; $Ph(CH_2)_4$, 5.35; PhMeCH, 0.111; PhEtCH, 0.0433; Ph_2CH, 0.0209; c-$C_6H_{11}CH_2$, 1.90	25	$10^3 k$, XCO_2-2-$C_{10}H_8$ + PrOH in PrOH at 40°, catalyzed by HCl[k] Me, 233; Pr, 69.2; $BuCH_2$, 64.4; t-Bu, 0.725
		26	$10^3 k$, XCO_2-2-$C_{10}H_8$ + i-PrOH in i-PrOH at 25°, catalyzed by HCl[k] Me, 5.43; Et, 2.62; Pr, 1.36; $BuCH_2$, 1.24; i-Pr, 0.300; t-Bu, 0.00595
		27	$10^3 k$, XCO_2-2-$C_{10}H_8$ + i-PrOH in i-PrOH at 40°, catalyzed by HCl[k] Me, 15.1; Et, 7.77; Pr, 3.80; $BuCH_2$, 3.55; i-Pr, 0.849; t-Bu, 0.0260
		28	$10^3 kr$, $XCO_2C_6H_4NO_2$-4 + H_2O in H_2O at 30°,[l] Me, 7.25; Et, 7.45; i-Pr, 4.33; Pr, 4.33; i-$PrCH_2$, 2.48; t-Bu, 0.884

[a] J. J. Sudborough and J. M. Gittins, *J. Chem. Soc.*, 93, 210 (1908); J. J. Sudborough and M. K. Turner, *ibid.*, 101, 237 (1912).
[b] J. J. Sudborough and L. L. Lloyd, *ibid.*, 75, 467 (1899). [c] C. N. Hinshelwood and A. R. Legard, *ibid.*, 1588 (1935). [d] H. A. Smith, *J. Amer. Chem. Soc.*, 61, 254 (1939); 62, 1136 (1940). [e] G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940). [f] H. A. Smith and J. H. Steele, *J. Amer. Chem. Soc.*, 63, 3466 (1941); H. A. Smith and R. R. Myers, *ibid.*, 64, 2362 (1942). [g] H. A. Smith and J. Burn, *ibid.*, 66, 1494 (1944). [h] E. W. Timm and C. N. Hinshelwood, *J. Chem. Soc.*, 862 (1938). [i] Not included in the correlation. [j] W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936). [k] M. Marfenist and R. Baltzly, *J. Amer. Chem. Soc.*, 69, 363 (1947). [l] T. H. Fife and D. M. McMahon, *ibid.*, 91, 7481 (1969).

served a linear relationship between $v_{CX_nH_{3-n}}$ and $v_{CM_nH_{3-n}}$. The necessary values are taken from Table III. They were correlated with the equation

$$v_{CX_nH_{n-3}} = m v_{CMe_3H_{n-3}} + c \qquad (7)$$

The results of the correlations with eq 7 are given in Table V. The sets studied are given in Table IV.

Of the seven sets correlated with eq 7, six (sets 52B, 53B, 54, 55B, 56, and 57) gave significant results. The correlations obtained permit a choice to be made between v values for the Cl_2CH group and the rejection of the value available for the Br_2CH group. New values were calculated from the correlations for the Br_2CH, F_2CH, and I_2CH groups. They are given in Table III.

The correlations of rate data for esterification and acid-catalyzed hydrolysis of esters with the v values answer the third of our objectives, the future examination of the Taft separation of polar and steric effects. We may now turn to an examination of the first of our purposes. Values of ψ and

S_ψ for the sets used by Taft to define E_s values are given in Table VI, as are also "Student t" tests for the significance of the difference between ψ for set 16 and the ψ values for the other sets. The results show clearly that the value of ψ for esterification of carboxylic acids in methanol at 25° (set 16) is significantly different from the other data used by Taft to define E_s values. Taft's E_s values must therefore be subject to some error. We may now turn our attention to our second objective, the validity of the hyperconjugation corrections introduced by Hancock and by Palm.

Sets 2 through 6 gave a very high degree of correlation with the v values which are based on the van der Waals radii. These sets included both the Me and the t-Bu substituents. The van der Waals radii are dependent only on group size and are completely independent of resonance effects of any type. Thus, although the Me and t-Bu groups should differ greatly in the amount of hyperconjugation they may give rise to, their effects on the rate are accounted for completely in terms of purely steric parameters. We are forced

Table II. Results of Correlations With Equation 6

Set	ψ	h	r^a	F^b	s_{est}^c	s_ψ^c	s_h^c	n^d
1	-2.23	3.10	0.9990	507.2[j]	0.0978	0.0992[j]	0.0845[h]	3
2	-2.33	1.79	0.9994	1591[e]	0.0460	0.0583[e]	0.0723[g]	4
3	-2.48	3.46	0.9996	1241[i]	0.0460	0.0705[h]	0.0785[h]	3
4	-2.14	2.78	0.9998	2761[i]	0.0358	0.0407[h]	0.0316[g]	3
5	-2.11	3.03	0.9999	3772[i]	0.0302	0.0343[h]	0.0266[g]	3
6	-2.05	3.22	0.9997	1959[i]	0.0408	0.0463[h]	0.0359[g]	3
7	-2.06	1.69	0.995	690.4[e]	0.0495	0.0784[e]	0.0615[e]	9
8	-1.98	2.03	0.995	658.0[e]	0.0486	0.0770[e]	0.0604[e]	9
9	-1.82	2.28	0.994	600.1[e]	0.0470	0.0743[e]	0.0583[e]	9
10	-1.79	1.22	0.975	193.3[e]	0.0508	0.129[e]	0.0990[e]	12
11	-2.49	1.93	0.991	491.6[e]	0.0857	0.112[e]	0.0920[e]	11
12	-1.80	1.62	0.978	218.6[e]	0.0479	0.122[e]	0.0933[e]	12
13	-1.78	1.99	0.976	203.6[e]	0.0492	0.125[e]	0.0959[e]	12
14	-1.74	2.32	0.975	189.4[e]	0.0499	0.127[e]	0.0973[e]	12
15	-1.96	2.35	0.9996	33409[e]	0.0184	0.0107[e]	0.0106[e]	26
16	-2.10	1.90	0.9995	3732[e]	0.0252	0.0344[e]	0.0307[e]	6
17	-1.12	2.24	0.991	52.54[k]	0.0328	0.155[k]	0.101[j]	3
18	-1.37	2.93	0.997	159.0[k]	0.0230	0.109[k]	0.0711[h]	3
19	-2.05	4.02	0.999	744.1[f]	0.0682	0.0753[g]	0.0757[e]	4
20	-1.92	4.51	0.99995	18811[e]	0.0127	0.0140[e]	0.0141[e]	4
21	-2.36	4.04	0.9995	2035[e]	0.0621	0.0522[e]	0.0502[e]	4
22	-2.94	4.09	0.997	637.9[e]	0.0678	0.117[e]	0.0906[e]	6
23	-4.14	4.07	0.996	138.8[k]	0.0639	0.352[k]	0.219[j]	3
24	-3.58	3.74	0.995	397.3[e]	0.105	0.180[e]	0.140[e]	6
25	-3.49	4.19	0.99991	10996[e]	0.0182	0.0333[e]	0.0275[e]	4
26	-4.06	2.78	0.993	283.6[e]	0.140	0.241[e]	0.187[e]	6
27	-3.79	3.06	0.991	215.6[e]	0.150	0.258[e]	0.200[e]	6
28	-1.25	1.54	0.988	157.0[e]	0.0612	0.0996[e]	0.0826[e]	6

[a] Correlation coefficient. [b] F test for significance of correlation. [c] Standard errors of the estimate, slope, and intercept. [d] Number of points in the set. [e] 99.9% CL (confidence level). [f] 99.5% CL. [g] 99.0% CL. [h] 98.0% CL. [i] 97.5% CL. [j] 95.0% CL. [k] 90.0% CL. [l] <90% CL. [m] 80% CL. [n] 50% CL. [o] 20% CL. [p] <20% CL.

Table III. Values of the Constants (v Values) Used in the Correlation

X	v	Source	X	v	Source
H	0	Ref 2	Pr$_2$CH	1.54	Sets 4, 5, 6
Me	0.52	Ref 2	Bu$_2$CH	1.56	Sets 4, 5, 6
t-Bu	1.24	Ref 2	(i-PrCH$_2$)$_2$CH	1.70	Sets 4, 5, 6
CCl$_3$	1.38	Ref 2	(t-BuCH$_2$)$_2$CH	2.03	Sets 4, 5, 6
CBr$_3$	1.56	Ref 2	i-PrCHEt	2.11	Sets 4, 5, 6
CI$_3$	1.79	Ref 2	t-BuCHMe	2.11	Sets 4, 5, 6
CF$_3$	0.91	Ref 2	t-BuCH$_2$CHMe	1.41	Sets 4, 5, 6
Me$_3$Si	1.40	Ref 2	c-C$_6$H$_{11}$	0.87	Sets 4, 5, 6
F	0.27	Ref 2	t-BuCMe$_2$	2.43	Sets 4, 5, 6
Cl	0.55	Ref 2	t-BuCH$_2$CMe$_2$	1.74	Sets 4, 5, 6
Br	0.65	Ref 2	Et$_3$C	2.38	Sets 4, 5, 6
I	0.78	Ref 2	PhCH$_2$	0.70	Sets 4, 5, 6
Ph	0.57	Ref 2	PhCH$_2$CH$_2$	0.70	Sets 4, 5, 6
	1.66[a]	Sets 4, 5, 6	Ph(CH$_2$)$_3$	0.70	Sets 4, 5, 6
Et	0.56	Sets 4, 5, 6	Ph(CH$_2$)$_4$	0.70	Sets 4, 5, 6
Pr	0.68	Sets 4, 5, 6	PhMeCH	0.99	Set 10
Bu	0.68	Sets 4, 5, 6	PhEtCH	1.18	Sets 4, 5, 6
BuCH$_2$	0.68	Sets 4, 5, 6	Ph$_2$CH	1.25	Sets 4, 5, 6
BuCH$_2$CH$_2$	0.73	Sets 7, 8, 9	ClCH$_2$	0.60	Set 2
Bu(CH$_2$)$_3$	0.73	Sets 7, 8, 9	BrCH$_2$	0.64	Set 2
Bu(CH$_2$)$_4$	0.68	Sets 4, 5, 6	Cl$_2$CH	1.28	Set 2
i-PrCH$_2$	0.98	Sets 4, 5, 6		0.81[a]	Set 21
t-BuCH$_2$	1.34	Sets 4, 5, 6	Br$_2$CH	1.32	Set 2
s-BuCH$_2$	1.00	Sets 4, 5, 6		0.89[a]	Set 53
i-PrCH$_2$CH$_2$	0.68	Sets 4, 5, 6	Br$_2$CMe	1.46	Set 2
t-BuCH$_2$CH$_2$	0.70	Sets 4, 5, 6	Me$_2$CBr	1.39	Set 2
t-BuCHEtCH$_2$CH$_2$	1.01	Sets 4, 5, 6	CH$_2$F	0.62	Set 7
c-C$_6$H$_{11}$CH$_2$	0.97	Sets 4, 5, 6	CH$_2$I	0.67	Set 2
c-C$_6$H$_{11}$CH$_2$CH$_2$	0.70	Sets 4, 5, 6	CH$_2$CN	0.89	Set 10
c-C$_6$H$_{11}$(CH$_2$)$_3$	0.71	Sets 4, 5, 6	CHI$_2$	0.97	Set 54
i-Pr	0.76	Sets 4, 5, 6	CHF$_2$	0.68	Set 51
s-Bu	1.02	Sets 4, 5, 6			
Et$_2$CH	1.51	Sets 4, 5, 6			
	1.28	Sets 7, 8, 9			

[a] Preferred values.

to the conclusion that alkyl groups exert only a steric effect on the esterification and acid-catalyzed hydrolysis of esters.

Nevertheless we have decided to compare the correlation of certain sets of data with the v, E_s, E_s^c, and E_s^o parameters. The sets chosen were 22-27 (Table I), which were originally examined by Hancock and coworkers[3] who compared correlations with E_s and E_s^c values, and 7, 8, and 9. The results of these correlations are presented in Table VII.

Table IV. CX_nH_{3-n} Sets (51–57)

Set: X:	51 F	52 Cl	53 Br	54 I	55 Et	56 Pr	57 Ph	Set: X:	51 F	52 Cl	53 Br	54 I	55 Et	56 Pr	57 Ph
$n = 0$	0.52	0.52	0.52	0.52	0.52	0.52	0.52	$n = 2$		1.28^a	1.32^c		1.51^d	1.54	1.25
1	0.62	0.60	0.64	0.67	0.68	0.68	0.70			0.81^b			1.28^e		
								3	0.91	1.38	1.56	1.79	2.38		

^{a} Included in set 52A. ^{b} Included in set 52B. ^{c} Included in set 53A, excluded in set 53B. ^{d} Included in set 55A. ^{e} Included in set 55B.

Table V. Results of Correlations with Equation 7

Set	m	c	r^a	F^b	$s_{est}{}^c$	$s_m{}^c$	$s_h{}^c$	n^d
51	0.491	0.304	0.980	24.35^l	0.0569	0.0994^m	0.0836^m	3
52A	1.16	0.0523	0.856	5.477^l	0.284	0.495^m	0.407^p	4
52B	1.17	−0.0762	0.9993	1524^e	0.0172	0.0301^e	0.0247^k	4
53A	1.39	−0.0609	0.904	8.925^k	0.266	0.466^k	0.382^p	4
53B	1.40	−0.179	0.998	31.59^j	0.0452	0.0790^j	0.0664^h	3
54	1.71	−0.331	0.998	288.2^j	0.0577	0.101^j	0.0848^m	3
55A	2.54	−0.680	0.978	44.89^i	0.217	0.378^j	0.311^m	4
55B	2.54	−0.743	0.997	336.2^f	0.0794	0.139^g	0.114^j	4
56	4.27	−1.70	0.99995	10364^g	0.00762	0.0419^g	0.0261^g	3
57	2.95	−0.985	0.997	145.4^k	0.0445	0.244^k	0.152^k	3

a–p See footnotes a–p, Table II.

Table VI. Test of Taft's Assumptions

Taft No.	Set	$-\psi$	s_ψ	t	CL	Taft No.	Set	$-\psi$	s_ψ	t	CL
1	11	2.49	0.112	11.34	99.9	3	3	2.48	0.0705	11.05	99.9
2	16	2.10	0.0344			4	21	2.36	0.0522	7.558	99.0

Table VII. Results of Correlations with the E_s, $E_s{}^c$, and $E°_s$ Steric Parameters

Set	δ	h	r^a	F^b	$s_{est}{}^c$	$s_\delta{}^c$	$s_h{}^c$	n^d
7A	0.868	1.34	0.995	689.7^e	0.0438	0.0331^e	0.0222^e	9
7B	0.577	1.41	0.977	145.6^e	0.0937	0.0479^e	0.0525^e	9
7C	0.659	1.40	0.986	242.7^e	0.0732	0.0423^e	0.0400^e	9
8A	0.944	1.01	0.997	1378^e	0.0337	0.0254^e	0.0170^e	9
8B	0.629	1.09	0.981	181.5^e	0.0914	0.0467^e	0.0512^e	9
8C	0.717	1.07	0.990	339.4^e	0.0674	0.0389^e	0.0368^e	9
9A	0.984	0.634	0.998	2008^e	0.0291	0.0220^e	0.0147^e	9
9B	0.655	0.715	0.981	177.7^e	0.0962	0.0491^e	0.0539^e	9
9C	0.747	0.697	0.990	336.0^e	0.0706	0.0408^e	0.0385^e	9
22A	1.37	2.54	0.992	255.1^e	0.107	0.0859^e	0.0596^e	6
22B	0.898	2.68	0.997	608.3^e	0.0694	0.0364^e	0.0429^e	6
22C	1.03	2.65	0.998	985.1^e	0.0546	0.0327^e	0.0329^e	6
23A	2.10	1.91	0.995	94.71^k	0.0773	0.215^k	0.0591^h	3
23B	0.969	2.00	0.994	77.22^k	0.0855	0.114^k	0.0729^j	3
23C	1.20	1.99	0.998	221.1^j	0.0507	0.0805^j	0.0424^h	3
24A	1.67	1.88	0.988	167.0^e	0.160	0.129^e	0.0895^e	6
24B	1.10	2.06	0.997	664.8^e	0.0810	0.0425^e	0.0500^e	6
24C	1.25	2.01	0.997	707.2^e	0.0786	0.0470^e	0.0473^e	6
25A	1.65	2.42	0.9992	1280^e	0.0533	0.0461^e	0.0376^e	4
25B	1.05	2.47	0.997	308.5^f	0.108	0.0595^g	0.0787^g	4
25C	1.20	2.46	0.998	426.4^f	0.0923	0.0580^g	0.0665^e	4
26A	1.89	0.665	0.985	133.7^e	0.203	0.163^e	0.113^g	6
26B	1.24	0.870	0.996	519.9^e	0.104	0.0545^e	0.0642^e	6
26C	1.42	0.820	0.996	480.9^e	0.108	0.0646^e	0.0650^e	6
27A	1.76	1.09	0.983	113.2^e	0.205	0.165^e	0.115^e	6
27B	1.16	1.28	0.996	525.7^e	0.0966	0.0507^e	0.0597^e	6
27C	1.32	1.24	0.995	419.4^e	0.108	0.0646^e	0.0650^e	6

a–k See footnotes a–k, Table II.

Sets correlated with E_s, $E_s{}^c$, and $E_s°$ are designated A, B, and C, respectively. The correlations were made with the equations

$$\log k_X = \delta E_{sX} + h \tag{8}$$

$$\log k_X = \delta^c E_{sX}{}^c + h^c \tag{9}$$

$$\log k_X = \delta° E_{sX}° + h° \tag{10}$$

The v values gave excellent correlations with both groups of data (sets 7–9 and sets 22–27), whereas the E_s values were slightly better with sets 7–9 but inferior with sets 22–27, and the $E_s{}^c$ and $E_s°$ values were slightly better with sets 22–27 but inferior with sets 7–9. Furthermore the v values make no assumptions concerning the existence of hyperconjugation effects, they are more simply defined than either $E_s{}^c$ or $E_s°$.

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It should further be noted that the respectable correlations obtained with $E_s{}^c$ and $E_s{}^9$ for sets 7-9 which supposedly include hyperconjugation effects that have been removed from $E_s{}^c$ and $E_s{}^o$ further suggest that hyperconjugation corrections are of very dubious validity. In our opinion, the v values are eminently suited for the correlation of steric effects upon rate and equilibria data and physical data as well. No "corrected" constants are necessary.

References and Notes
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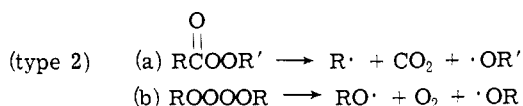(6) M. Charton, Progr. Phys. Org. Chem., 10, 81 (1973).

Concerted Mechanism and Phase Effects in Decompositions of Alkyl Peroxy Esters[1]

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Abstract: Two primary alkyl peroxyacetates (n-butyl and isobutyl) and two secondary peroxyacetates (sec-butyl and cyclohexyl) were prepared and their liquid and gas-phase decomposition rates and products compared with those of tert-butyl peroxyacetate. Thermal, liquid-phase, decompositions of the primary and secondary peroxy esters, either pure, in chlorobenzene solution, or in α-methylstyrene solution, yielded mainly acetic acid and the aldehyde or ketone corresponding to the alcohol moiety of the ester (E_{act} = 24-28 kcal/mol, log A = 10-12). Both products and kinetics are in accord with a concerted six-centered mechanism analogous to the pyrolytic decomposition of esters. By contrast, thermal decomposition of n-butyl peroxyacetate in the vapor phase gives products and kinetic parameters (E_{act} = 36.0 kcal/mol, log A = 16.0) indicative of a simple O-O homolysis. In this respect, the vapor-phase decomposition of n-butyl peroxyacetate corresponds to the homolytic decomposition of tert-butyl peroxyacetate both in the liquid and vapor phase (E_{act} = 35.8 kcal/mol, log A = 16.1). The striking difference between liquid- and gas-phase thermal decomposition of n-butyl peroxyacetate parallels previous observations of peroxide decompositions involving a concerted hydrogen transfer and may be general for this class of reactions. We tentatively conclude that the cyclic concerted reaction proceeds via a transition state with significant ionic character which is solvent stabilized, thereby lowering the energy of activation of the liquid phase decomposition. In the gas phase, without this solvent stabilization of the cyclic concerted transition state, the normal homolytic cleavage of the O-O bond takes precedence.

It seems useful to describe three categories for the nonheterolytic decompositions of organic peroxides. The first, simple O-O homolysis (type 1), needs no amplification. The second, concerted multiple bond homolysis (type 2a), is most popularly exemplified by pyrolyses of tert-alkyl peroxy esters[4] and can be extended to the scission of tert-butyl tetroxide,[5,6] (type 2b). Our main focus here will be on what we shall label type 3 decompositions, the cyclic concerted, six-center cleavage and its relevance to the decomposition of nontertiary alkyl peroxy esters. Typical of this category is the "Russell Mechanism"[7] (type 3a) for the breakdown of nontertiary tetroxides,[8] the formation of H_2 from certain alkylidene peroxides[9] (type 3b), the decomposition of sec-alkyl peroxides[10] (type 3b), and the decomposition of nontertiary peroxy esters[11] (type 3c), the subject of this paper.

(type 1) $ROOR \longrightarrow 2RO\cdot$

(type 2)   (a) $RCOOR' \longrightarrow R\cdot + CO_2 + \cdot OR'$

(b) $ROOOOR \longrightarrow RO\cdot + O_2 + \cdot OR$

An intriguing aspect of this type of reaction is its apparent preference for the liquid phase. Thus peroxides which yield substantial amounts of H_2 when decomposed in solution give little or none on vapor-phase pyrolysis.[10,12] This is not to say that type 1 or type 2 reactions do not compete with type 3 in the liquid phase; they clearly do;[8a,8b,9b,10] however, reactions of type 3 appear to be favored in the liquid phase vs. the vapor phase.[12] An exception may be the type 3a reaction. Recent comparative studies of liquid and

gas phase n-butane oxidations indicate very little differences in rate and products for the primary reaction with phase change. These results are compatible with the same radical-terminating process involving a type 3a reaction in each.[13]

(type 3) (a)

(b)

(b′)

(c)
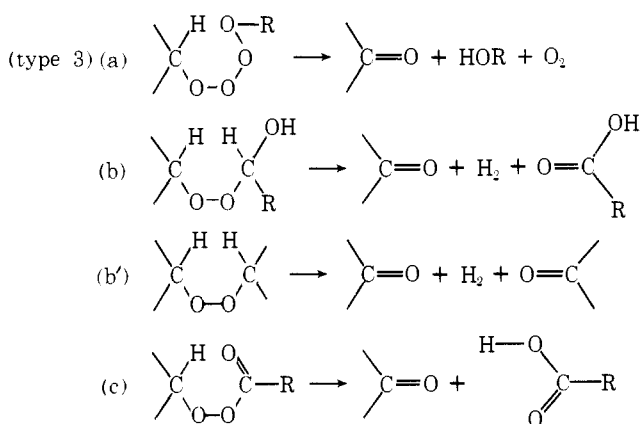
Beyond the preliminary communication[11] and thesis[3] which proposed a type 3c decomposition for primary and secondary alkyl peroxy esters in the liquid phase, such species have received very little attention.[14,15] The full details of that earlier report are presented here, together with an account of broader aspects of the chemistry of these compounds. Vapor-phase studies have been included in order to expand the data to include the differences between liquid and gas-phase peroxy ester decompositions. The gas-