and immediately adding CCl_4 to the residue, IR 1735 cm^{-1} (C═O); NMR δ 2.38 (d, J_{FCH_3} = 4), 2.18 (d, J_{FCH_3} = 20). The compound decomposes after 2 days even when kept in CCl_4. The diastereoisomeric (−)-menthydrazone prepared in CCl_4 solution had mp 162–164 °C dec. Anal. Calcd for $C_{15}H_{26}FIN_2O_2$: C, 49.08; H, 7.07. Found: C, 50.69; H, 6.50. Attempted preparation of the title compound in ethanol as solvent gave decomposed mixtures. No reaction occured without the use of any solvent.

Other iodo compounds which were prepared by the same general method but could not be isolated in pure form due to their instability were: 1-Iodo-1-phenyl-2-propanone (98%): IR 1715 cm^{-1} (C═O); NMR δ 2.35 (s), 7.32 (m). 2-Iodo-1-phenyl-1-propanone (26.5%): IR 1693 cm^{-1} (C═O); NMR δ 2.10 (d, J_{HCH_3} = 6), 6.10 (q, J_{HCH_3} = 6), 7.65 (m). 1-Chloro-1-iodo-1-phenyl-2-propanone (96%): IR 1733 cm^{-1} (C═O); NMR δ 2.35 (s), 7.38 (m). 2-Chloro-2-iodo-1-phenyl-1-propanone (13%): IR 1695 cm^{-1} (C═O); NMR δ 2.40 (s), 7.75 (m). 1-Fluoro-1-iodo-1-phenyl-2-propanone (95%): IR 1723 cm^{-1} (C═O); NMR δ 2.30 (d, J_{FCH_3} = 4), 7.40 (m). 2-Fluoro-2-iodo-1-phenyl-1-propanone (35%): IR 1696 cm^{-1} (C═O); NMR δ 2.54 (d, J_{FCH_3} = 20), 7.78 (m). 1-Bromo-1-iodo-1-phenyl-2-propanone (98%) [IR 1720 cm^{-1} (C═O); NMR δ 2.30 (s), 7.60 (m)] and 2-bromo-2-iodo-1-phenyl-1-propanone (68%) [IR 1690 cm^{-1} (C═O); NMR δ 2.35 (s), 7.60 (m)] were also prepared by bromination of the corresponding iodo-compounds with NBS in the general manner.

Registry No.—**1a** semicarbazone, 63017-11-8; **1a** (−)-menthydrazone epimer I, 63017-12-9; **1a** (−)-menthydrazone epimer II, 63017-13-0; **1c**, 63017-14-1; **1c** (−)-menthydrazone epimer I, 63017-15-2; **2c** (−)-menthydrazone epimer II, 63017-16-3; **2b′**, 63017-17-4; **3a** (−)-menthydrazone epimer I, 63017-18-5; **3a** (−)-menthydrazone epimer II, 63017-19-6; **3c**, 63017-20-9; 1,3-difluoro-2-butanone, 63058-87-7; **4b′**, 703-17-3; **6a′** semicarbazone, 63017-21-0; **6a′** (−)menthydrazone epimer I, 63017-22-1; **6a** (−)-menthydrazone epimer II, 63017-23-2; **10a** (−)-menthydrazone epimer I, 63017-24-3; **10a** (−)-menthydrazone epimer II, 63017-25-4; 2 chloro-1-phenyl-2-propen-1-one, 19233-44-4; 3-chloro-1-fluoro-1-phenyl-2-propanone, 63017-26-5; 3-chloro-1-bromo-1-fluoro-1-phenyl-2-propanone, 63017-27-6; 2,2-dichloro-1-phenyl-1-propanone, 57169-51-4; 3-iodo-2-butanone, 30719-18-7; 3-bromo-2-butanone, 814-75-5; 3-iodo-2-butanone (−)-menthydrazone epimer I, 63017-28-7; 3-iodo-2-butanone (−)-menthydrazone epimer II, 63017-29-8; 3-iodo-2-butanone semicarbazone, 63017-30-1; 3-brono-3-iodo-2-butanone, 63017-31-2; 3-bromo-3-iodo-2-butanone (−)-menthydrazone epimer I, 63017-32-3; 3-bromo-3-iodo-2-butanone (−)-menthydrazone epimer II, 63067-33-4; 3-chloro-3-iodo-2-butanone, 63017-34-5; 3-chloro-3-iodo-2-butanone (−)-menthydrazone epimer I, 63058-88-8; 3-chloro-3-iodo-2-butanone (−)-menthydrazone epimer II, 63017-35-6; 3-chloro-3-iodo-2-butanone semicarbazone, 63107-36-7; 3-fluoro-3-iodo-2-butanone, 63017-37-8; 3-fluoro-3-iodo-2-butanone (−)-menthydrazone epimer I, 63017-38-9; 3-fluoro-3-iodo-2-butanone (−)-menthydrazone epimer II, 63017-39-0; 1-iodo-1-phenyl-2-propanone, 63017-40-3; 2-iodo-1-phenyl-1-propanone, 6084-15-7; 1-chloro-1-iodo-1-phenyl-2-propanone, 63017-41-4; 2-chloro-2-iodo-1-phenyl-1-propanone, 63017-42-5; 1-fluoro-1-iodo-1-phenyl-2-propanone, 63017-43-6; 2-fluoro-2-iodo-1-phenyl-1-propanone, 63017-44-7; 1-bromo-1-iodo-1-phenyl-2-propanone, 63017-45-8; 2-bromo-2-iodo-1-phenyl-1-propanone, 63017-46-9.

References and Notes

(1) R. A. Cox and J. Warkentin, *Can. J. Chem.*, **50,** 3242 (1972).
(2) N. Sokolowsky, *Ber.*, **9,** 1687 (1876).
(3) J. F. Norris. *J. Ind. Eng. Chem.*, **11,** 828 (1919).
(4) F. Swarts, *Bull. Cl. Sci., Acad. R. Belg.*, **13,** 175 (1927).
(5) R. A. Darrall, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2329 (1951); A. Sykes, J. C. Tatlow, and C. R. Thomas, *ibid.*, 835 (1956).
(6) E. T. McBee, O. R. Pierce, H. W. Kolbourne, and E. R. Wilson, *J. Am. Chem. Soc.*, **75,** 3152 (1953); E. T McBee, O. R. Pierce, and D. D. Meyer, *ibid.*, **77,** 917 (1955).
(7) K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78,** 2268 (1956).
(8) R. A. Shepard and A. A. Loiselle, *J. Org. Chem.*, **23,** 2012 (1958).
(9) F. Swarts, *Bull. Acad. R. Belg.*, **54,** (1895); *Bull. Soc. Chim. Fr.*, **15,** 1134 (1896); *Bull. Cl. Sci., Acad. R. Belg.*, **35,** 849 (1898).
(10) A. L. Henne and T. Midgley Jr., *J. Am. Chem. Soc.* **58,** 882 (1936).
(11) F. Swarts, *Bull. Acad. R. Belg.*, 731 (1902); *Chem. Zentralbl. I*, 437 (1903).
(12) E. D. Bergman, *J. Chem. Soc.*, 3457 (1961).
(13) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96,** 2250 (1974).
(14) R. Nouri-Bimorghj, *Bull. Soc. Chim. Fr.*, **11,** 3178 (1965).
(15) D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29,** 1956 (1964).
(16) R. Poggi, *Gazz, Chem. Ital.*, **70,** 328 (1940).
(17) C. Djerassi and C. T. Lenk, *J. Am. Chem. Soc.*, **75,** 3493 (1953).
(18) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Am. Chem. Soc.*. **63,** 120 (1941).
(19) E. D. Kosower, W. J. Cole, E. D. Cardy, and G. Meisters. *J. Org. Chem.*, **28,** 630 (1963).
(20) J. P. Schaefer and F. Sonnenberg, *J. Org. Chem.*, **28,** 1128 (1963).
(21) D. P. Shirkov, T. V. Smirnova, and A. N. Litvinova, *Zh. Vses, Khim. Ova.*, **14,** 234 (1969).
(22) H. Newman and R. B. Angier, *Tetrahedron*, **26,** 825 (1970).
(23) C. Rapp and R. Kumar, *Ark. Kemi*, **23,** 475 (1965).
(24) S. Wolfe, W. R. Pilgrim, T. F. Carrard, and P. Chamberlain, *Can. J. Chem.*, **49,** 1099 (1971).
(25) R. F. Merritt and T. K. Ruff, *J. Org. Chem.*, **30,** 328 (1965).
(26) J. Cantacuzene and J. Leroy, *Tetrahedron Lett.*, **37,** 3277 (1970).
(27) M. Ballester and J. Riera, *An. R. Soc Esp. Fis. Quim.*, **56,** 897 (1960).

Steric Effects. 9. Substituents at Oxygen in Carbonyl Compounds

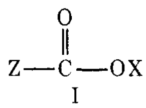
Marvin Charton

Department of Chemistry, Pratt Institute, Brooklyn, New York 11205

Received January 20, 1976

Twenty-nine sets of basic hydrolyses rate constants for alkyl acetates, formates, propionates, and benzoates; four sets of acid-catalyzed hydrolysis rate constants of alkyl acetates; one set of rate constants for the vapor-phase esterification of acetic acid with alcohols; and one set of rate constants for the reaction of 4-nitrobenzoyl chloride with alcohols were correlated by the modified Taft equation using υ_X, υ_{CH_2X}, and υ_{OX} constants. Best results were obtained with the υ_{OX} constants which were defined in this work. Forty values of υ_{OX} are given. The successful correlation with υ_{CH_2X} verified the validity of the equation $\upsilon_{Z_1X} = \upsilon_{Z_2X} + c$. The magnitude of ψ as a function of the structure of the substrate is described.

In many data sets of reaction rates of carbonyl compounds, the effect of substitution at an oxygen atom has been studied. In particular, rates of ester hydrolysis of I, where Z is a constant substituent and X is permitted to vary, have been examined. The first attempt at handling steric effects of the X group is due to Taft,[1] who proposed E_S values for these groups and pointed out[2] that E_{SX} and E_{SZ} may differ significantly from each other when X = Z. In this work, effects of R in the set RCH_2OAc were correlated with the Taft equation



$$Z{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OX$$

I

$$\log (k/k^0) = \delta E_S \tag{1}$$

using E_{SZ} values. Results were good for a set of eight substituents, although two of the substituents had to be excluded from the set. It seemed to us of interest to extend our previous investigation[3-10] to this topic. For this purpose, we examined

Table I. Data Used in the Correlations

1. *kr*, ROBz + OH^- in 56% w/w MeAc–H_2O at 25 °C[a]
   Me, 9.022; Et, 2.891; Pr, 1.932; Bu, 1.667; $BuCH_2CH_2$, 1.274; $Bu(CH_2)_4$, 1.263; *i*-Pr, 0.4644; *i*-Bu, 1.429; *s*-Bu, 0.2259; *t*-Bu, 0.01327; *i*-$PrCH_2CH_2$, 1.200; MePrCH, 0.1487; Me_2EtC, 0.005024;[b] *c*-C_5H_9, 0.3972; c-C_6H_{11}, 0.2679
2. *kr*, ROBz, + OH^- in 60% v/v dioxane–H_2O at 35 °C[c]
   Me, 1.74; Et, 0.553; Pr, 0.379; *i*-Pr, 0.0919; Bu, 0.289; *i*-Bu, 0.240; *s*-Bu, 0.0468; *i*-$PrCH_2CH_2$, 0.234; Et_2CH, 0.0162
3. *kr*, ROAc + OH^- in 40% v/v dioxane–H_2O at 35 °C[d]
   Me, 19.3; Et, 8.90; Pr, 6.75; *i*-Pr, 1.84; Bu, 5.38; *i*-Bu, 3.95; *s*-Bu, 0.954; *t*-Bu, 0.103;
4. *kr*, ROAc + OH^- in 62% w/w MeAc–H_2O at 0 °C[e]
   Me, 0.910; Et, 0.405; *i*-Pr, 0.0628; *i*-Bu, 0.147
5. *kr*, ROAc + OH^- in 62% w/w MeAc–H_2O at 10 °C[e]
   Me, 2.08; Et, 0.908; *i*-Pr, 0.1395; *i*-Bu, 0.314
6. *kr*, ROAc + OH^- in 62% w/w MeAc–H_2O at 20 °C[e]
   Me, 3.96; Et, 1.75; *i*-Pr, 0.289; *i*-Bu, 0.676
7. 10^4 *kr*, ROAc + H_3O^+ in 62% w/w MeAc–H_2O at 30.1 °C[e]
   Me, 52.0; Et, 42.6; *i*-Pr, 20.0; *i*-Bu, 30.9; *t*-Bu, 8.00
8. 10^4*kr*, ROAc + H_3O^+ in 62% w/w MeAc–H_2O at 40 °C[e]
   Me, 120.0; Et, 98.5; *i*-Pr, 47.1; *i*-Bu, 71.6; *t*-Bu, 27.0
9. 10^2*kr*, ROAc + OH^- in 70% v/v MeAc–H_2O at 20 °C[f]
   Me, 8.47; Et, 3.56; Pr, 2.02; *i*-Pr, 0.530; *i*-Bu, 1.41; Bu, 1.74; *s*-Bu, 0.231
10. 10^2*kr*, ROAc + OH^- in 70% v/v MeAc–H_2O at 24.7 °C[f]
    Me, 10.8; Et, 4.66; Pr, 2.70; *i*-Pr, 0.706; *i*-Bu, 1.82; Bu, 2.30; *s*-Bu, 0.327; *t*-Bu, 0.0265; c-C_6H_{11}, 0.456
11. 10^2*kr*, ROAc + OH^- in 70% v/v MeAc–H_2O at 35 °C[f]
    Et, 8.22; Pr, 5.07; *i*-Pr, 1.40; *i*-Bu, 3.55; Bu, 4.39; *s*-Bu, 0.682; *t*-Bu, 0.0593; *c*-C_6H_{11}, 0.884
12. 10^2*kr*, ROAc + OH^- in 70% v/v MeAc–H_2O at 44.7 °C[f]
    Et, 13.5; Pr, 8.80; *i*-Pr, 2.53; *i*-Bu, 6.28; Bu, 7.66; *s*-Bu, 1.27; *t*-Bu, 0.112; c-C_6H_{11}, 1.78
13. 10^2*kr*, RO_2CEt + OH^- in 70% v/v MeAc–H_2O at 20 °C[f]
    Me, 4.93; Et, 1.65; *i*-Pr, 0.201; Bu, 0.760
14. 10^2*kr*, RO_2CEt + OH^- in 70% v/v MeAc–H_2O at 24.7 °C[f]
    Me, 6.41; Et, 2.21; *i*-Pr, 0.298; Bu, 0.989
15. 10^2*kr*, RO_2CEt + OH^- in 70% v/v MeAc–H_2O at 35 °C[f]
    Me, 10.9; Et, 4.08; *i*-Pr, 0.604; Bu, 1.88
16. 10^2*kr*, RO_2CEt + OH^- in 70% v/v MeAc–H_2O at 44.7 °C[f]
    Me 17.5; Et, 6.84; *i*-Pr, 1.14; Bu, 3.51
17. *kr*, RO_2CH + OH^- in H_2O at 5 °C[g]
    Me, 696; Et, 509; Pr, 483; Bu, 456; *i*-Pr, 239
18. *kr*, RO_2CH + OH^- in H_2O at 15 °C[g]
    Me, 1240; Et, 902; Pr, 844; Bu, 789; *i*-Pr, 413
19. *kr*, RO_2CH + OH^- in H_2O at 25 °C[g]
    Me, 2200; Et, 1540; Pr, 1370; Bu, 1310; *i*-Pr, 655
20. *kr*, RO_2CH + OH^- in H_2O at 35 °C[g]
    Me, 3730; Et, 2440; Pr, 2170; Bu, 1840; *i*-Pr, 1040
21. *kr*, ROH + AcOH over silica–alumina catalyst at 250 °C[h]
    Me, 6.6; Et, 6.3; Pr, 8.0; Bu, 8.2; *i*-Bu, 7.8; *i*-Pr, 5.5; *s*-Bu, 8.3; *t*-Bu, 14.0
22. 10^3*kr*, ROH + 4-$O_2NC_6H_4COCl$ in Et_2O at 25 °C[i]
    Me, 184; Et, 84.5; Pr, 65.9; *i*-Pr, 10.1; Bu, 70.3; *s*-Bu, 7.35; *t*-Bu, 2.70; *i*-Bu, 30.8; $BuCH_2$, 79; $BuCH_2CH_2$, 85; $Bu(CH_2)_3$, 69; *s*-$BuCH_2$, 36; *i*-$PrCH_2CH_2$, 73; *i*-$PrCH_2CH_2CH_2$, 68; MePrCH, 5.9; MeBuCH, 6.5; Et_2CH, 3.6; Pr_2CH, 2.7
23. 10^5*kr*, ROAc + H_3O^+ in 75% v/v MeAc–H_2O at 35 °C catalyzed by HCl[j]
    Me, 13.0; Et, 12.0; Bu, 9.65; c-C_5H_9, 4.35; PrMeCH, 3.59; $BuCH_2$, 8.78; c-C_6H_{11}, 3.79; $BuCH_2CH_2$, 7.60; $Bu(CH_2)_4$, 6.65
24. 10^5*kr*, ROAc + H_3O^+ in 75% v/v MeAc–H_2O at 35 °C catalyzed by resin acid[j]
    Me, 6.45; Et, 3.34; Bu, 1.12; c-C_5H_9, 0.612; PrMeCH, 0.308; $BuCH_2$, 0.663; c-C_6H_{11}, 0.478; $BuCH_2CH_2$ 0.420; $Bu(CH_2)_4$, 0.083
25. *kr*, ROAc + OH^- in H_2O at 20.0 °C, average values[k]
    Me, 8.09; Et, 4.85; *i*-Pr, 1.29; Bu, 4.05; $BuCH_2$, 3.63; *i*-$PrCH_2CH_2$, 3.17
26. *kr*, ROAc + OH^- in H_2O at 30.0 °C, average values[k]
    Me, 16.0; Et, 9.04; *i*-Pr, 3.40; Bu, 7.41; $BuCH_2$, 6.82; *i*-$PrCH_2CH_2$, 6.49
27. *kr*, ROAc + OH^- in H_2O at 20 °C and 2000 atm[k]
    Bu, 6.1; *i*-Bu, 5.7; *i*-Pr, 2.08; $BuCH_2$, 6.0
28. *kr*, ROAc + OH^- in H_2O at 20 °C and 5000 atm[k]
    Et, 15.9; Bu, 14.1; *i*-Bu, 12.3; *i*-Pr, 5.2
29. *kr*, ROAc + OH^- in H_2O at 20 °C and 8000 atm[k]
    Et, 31.0; Bu, 25.7; *i*-Bu, 28.3; *i*-Pr, 11.4; $BuCH_2$, 25.2
30. 10^3*kr*, ROAc + OH^- in 70% v/v dioxane–H_2O at 20 °C[l]
    Me, 54; Et, 35; *s*-$BuCH_2$, 12.5; *i*-$PrMeCHCH_2$, 10; *t*-$BuCH_2$, 8.6; $EtMe_2CCH_2$, 6.0; *i*-$PrEtCHCH_2$, 5.3; Et_2CHCH_2, 5.1; $BuEtCHCH_2$, 5.1; *t*-$BuEtCHCH_2$, 1.7; Et_3CCH_2, 1.5; c-$C_3H_5CH_2$, 31; c-$C_4H_7CH_2$, 23; c-$C_5H_9CH_2$, 16; c-$C_6H_{11}CH_2$, 10.
31. 10^3*kr*, ROAc + OH^- in 70% v/v dioxane–H_2O at 30 °C[l]
    Et, 66; *s*-$BuCH_2$, 27; *t*-$BuCH_2$, 17; c-$C_6H_{11}CH_2$, 23; *i*-Pr, 12.4; *t*-Bu, 0.8
32. *kr*, ROAc + OH^- in H_2O at 0.0 °C[m]
    Pr, 1.01; *i*-Pr, 0.313; Bu, 0.925; *i*-Bu, 0.870; *s*-Bu, 0.206; *t*-Bu, 0.0158; *i*-$PrCH_2CH_2$, 0.899
33. *kr*, ROAc + OH^- in H_2O at 10.0 °C[m]
    Pr, 2.15; *i*-Pr, 0.640; Bu, 1.94; *i*-Bu, 1.76; *s*-Bu, 0.419; *t*-Bu, 0.0368; *i*-$PrCH_2CH_2$, 1.80
34. *kr*, ROAc + OH^- in H_2O at 20.0 °C[m]
    Me, 7.84; Et, 4.57; Pr, 4.23; *i*-Pr, 1.26; Bu, 3.93; *i*-Bu, 3.54; *s*-Bu, 0.816; *t*-Bu, 0.0809; *i*-$PrCH_2CH_2$, 3.61; Et_2CH, 0.340; Me_2EtC, 0.0374
35. *kr*, ROAc + OH^- in H_2O at 30.0 °C[m]
    Pr, 8.09; *i*-Pr, 2.50; Bu, 7.58; *i*-Bu, 6.75; *s*-Bu, 1.55; *t*-Bu, 0.166; *i*-$PrCH_2CH_2$, 6.72

[a] E. Tommila, *Ann. Acad. Sci. Fenn., Ser. A3,* **59,** 3–34 (1942); *Chem. Abstr.*, **38,** 6172*b* (1944). [b] Excluded from correlation. [c] C. K. Hancock and C. P. Falls, *J. Am. Chem. Soc.*, **83,** 4214 (1961). [d] C. K. Hancock, E. A. Meyers, and B. J. Yager, *J. Am. Chem. Soc.*, **83,** 4211 (1961). [e] R. N. Rylander and D. S. Tarbell, *J. Am. Chem. Soc.*, **72,** 3021 (1950). [f] R. W. A. Jones and J. D. R. Thomas, *J. Chem. Soc. B,* 661 (1966). [g] R. Leimu, R. Korte, E. Laaksonen, and V. Lehmuskoski, *Suom. Kemistil. B,* **19,** 93 (1946). [h] I. Mochida, Y. Anju, A. Kato, and T. Seiyama, *Bull. Chem. Soc. Jpn.*, **44,** 2326 (1971). [i] J. F. Norris and A. A. Ashdown, *J. Am. Chem. Soc.*, **47,** 837 (1925); J. F. Norris and F. Cortese, *ibid.*, **49,** 2340 (1927). [j] S. Affrossman and J. P. Murray, *J. Chem. Soc. B,* 579 (1968). [k] B. Anderson, F. Gronlund, and J. Olsen, *Acta Chem. Scand.*, **23,** 2458 (1969). [l] S. Sarel, L. Tsai, and M. S. Newman, *J. Am. Chem. Soc.*, **78,** 5420 (1956). [m] L. Smith and H. Olsson, *Z. Phys. Chem.*, **118,** 99 (1925); H. Olsson, *ibid.*, **118,** 107 (1925); **125,** 243 (1927).

the correlation of rate constants for 29 sets of base-catalyzed hydrolysis and four sets of acid-catalyzed hydrolysis of esters of the type I with the modified Taft equation,

$$\log k_{\mathrm{OX}} = \upsilon_{\mathrm{X}} + h \qquad (2)$$

Also studied were a set of rate constants for the reaction of XOH with AcOH, and a set of rate constants for the reaction of XOH with 4-$O_2NC_6H_4COCl$. The data used in the correlations are presented in Table I. The υ constants required for the correlations are from our previous work.[3,9] For results of the correlations with eq 2, see the paragraph at the end of the paper. In this work only substituents OX with X = alkyl have been examined. Alkyl substituents even in basic hydrolysis seem to be free of variable electrical effects, as we have shown for esters in which X is constant and Z is alkyl.[4] As further evidence, consider the σ_I and σ_R constants of alkoxy substituents. For values of these, see the paragraph at the end of this paper.

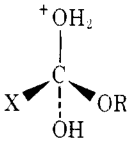
Results of the correlations with eq 2 are as follows: nine sets gave excellent (>99.5% CL), one gave very good (99.0% CL),

Table II. Calculated Values of υ_{OMe}

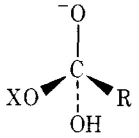
υ_{OMe}	Set	Ref
0.43	2	*a*
0.30	6	*b*
0.30	2A	*c*

[a] M. Charton, *J. Org. Chem.*, **40**, 407 (1975). [b] Reference 7. [c] Reference 10.

nine gave good (97.5% CL), eight gave fair (95.0% CL), and one gave poor correlation (90.0% CL). Seven sets did not give significant results (<90.0% CL). As the large majority (28 out of 35) of the sets studied gave significant results, it seems reasonable to conclude that the data studied involve predominantly steric effects. The υ_X values do not seem to be the best steric parameter for representing the data, however. If we examine the tetrahedral intermediate for the basic ester hydrolysis reactions which constitute most of the sets studied (1–6, 9–20, 25–35) and compare it with the tetrahedral intermediate from which υ_X values are defined, II and III, respectively, we observe that as R remains constant X varies in II and OX in III. What is required then is a set of υ_{OX} values. Such values are unavailable. The correlations obtained with υ_X did not seem to us to be good enough to use as the basis for the definition of υ_{OX} values. We have therefore examined the following approach to the problem. Consider a substituent to be composed of two parts, Z and X, where Z joins X and the skeletal group G to which the substituent is attached. Now let us assume that for some substituent Z_1X we can write the steric parameter υ as,



II



III

$$\upsilon_{Z_1X} = f_{Z_1} + f_X \tag{3}$$

while for some other substituent, Z_2X we can write

$$\upsilon_{Z_2X} = f_{Z_2} + f_X \tag{4}$$

Then,

$$\upsilon_{Z_1X} = \upsilon_{Z_2X} + f_{Z_1} - f_{Z_2} \tag{5}$$

If we consider two sets of substituents, one with constant Z_1 and the other with constant Z_2,

$$\upsilon_{Z_1X} = \upsilon_{Z_2X} + c \tag{6}$$

Then from eq 7, with $Z_1 = CH_2$ and $Z_2 = O$

$$\upsilon_{OX} = \upsilon_{CH_2X} + c \tag{7}$$

We have therefore correlated the data in Table I with the equation

$$\log k_{OX} = \psi\upsilon_{CH_2X} + h \tag{8}$$

For the results of the correlations with eq 8, see the paragraph at the end of this paper. Nineteen sets gave excellent (>99.5% CL), four gave very good (99.0% CL), four gave good (97.5% CL), and six gave poor correlation (90% CL). One set did not give significant results (<90.0% CL). Obviously, the results obtained from correlation with eq 8 are very much better than those obtained with eq 2. Ideally, however, we would like to have a set of υ_{OX} values. It is essential to be able to employ these υ_{OX} values together with the other υ values we have determined, so that data sets containing many different substituent types can be correlated with the modified Taft equation. It is particularly important, therefore, that the υ_{OX} values be on the same scale as the υ values we have previously reported. If this is not done, then the utility of the υ_{OX} steric parameters would be limited to sets including only OX groups, and the parameters would be much less useful. We may now proceed to define such a set of values. For this purpose, we must choose a reference set of data, a value for some OX substituent, and a value of ψ for the reference set. For a reference set, we have chosen set 10, rate constants for the basic hydrolysis of alkyl acetates in 70% v/v MeAc–H$_2$O at 24.7 °C. This set was chosen because it gave an excellent correlation with eq 8 and included many of the most common OX groups. We then assigned a value of 0.36 to υ_{OMe}. This value was chosen on the basis that $\upsilon_{OH} = 0.32$, $\upsilon_{CH_2Me} = 0.56$, and $\upsilon_{CH_3} = 0.52$. Then the effect of replacing H with Me in CH$_2$Me = $\upsilon_{CH_2Me} - \upsilon_{CH_3} = 0.04$. Therefore, the effect of replacing H by Me for OMe should also be 0.04, and $\upsilon_{OMe} - \upsilon_{OH} = 0.04$. Then, it follows that υ_{OMe} should be about 0.36. Values of υ_{OMe} obtained from other correlations in previous investigations are shown in Table II. The average value of υ_{OMe} obtained is 0.34, in good agreement with the value of 0.36 we have chosen. The value of ψ chosen is the value obtained for the correlation set 10 with eq 8 in order to place the υ_{OX} values on the same scale

Table III. υ_{OX} Values

OX	υ	Source	OX	υ	Source
OMe	0.36	definition	OCH$_2$CMe$_2$Et	0.78	31
OEt	0.48	10	OCH$_2$CHEt-*i*-Pr	0.76	31
OPr	0.56	10	OCH$_2$CHEt$_2$	0.71	31
O-*i*-Pr	0.75	10	OCH$_2$CHEtBu	0.76	31
O-*i*-Bu	0.62	10	OCH$_2$CHEt-*t*-Bu	0.96	31
OBu	0.58	10	OCH$_2$CEt$_3$	0.97	31
O-*s*-Bu	0.86	10	OCH$_2$-c-C$_3$H$_5$	0.48	31
O-*t*-Bu	1.22	10	OCH$_2$-c-C$_4$H$_7$	0.52	31
O-c-C$_6$H$_{11}$	0.81	10	OCH$_2$-c-C$_5$H$_9$	0.58	31
OCH$_2$CH$_2$Bu	0.61	1	OCH$_2$-c-C$_6$H$_{11}$	0.65	31
O(CH$_2$)$_4$Bu	0.61	1	OCHMe-*i*-Pr	0.91	31
OCH$_2$CH$_2$-*i*-Pr	0.62	1	OCHEt-*i*-Pr	1.18	31
OCH$_2$MePr	0.90	1	OCHMe-*t*-Bu	1.19	31
OCMe$_2$Et	1.35	1	OCHiBu$_2$	1.28	31
O-c-C$_5$H$_9$	0.77	1	OCH$_2$CH$_2$-*t*-Bu	0.53	30
OCHEt$_2$	1.00	2	OCH$_2$CHMe-*t*-Bu	0.66	30
OCH$_2$Bu	0.58	26	OCH$_2$CMeEt$_2$	0.82	30
OCH$_2$-*s*-Bu	0.62	31	OCH$_2$CH-*i*-Pr$_2$	0.89	30
OCH$_2$CHMe-*i*-Pr	0.64	31	OCEt$_2$Me	1.52	34
OCH$_2$-*t*-Bu	0.70	31	OCPrMe$_2$	1.39	34

Table IV. Values of ψ, h, and $100r^2$ Obtained from Correlation with Equation 10

Set	$-\psi$	h	$100r^2$	Set	$-\psi$	h	$100r^2$
1	3.25	2.10	99.8	19	1.31	3.83	96.4
2	3.08	1.29	99.2	20	1.40	4.08	98.6
3	2.65	2.26	99.8	21	−0.369	0.667	87.6
4	3.00	1.04	100.	22	2.17	2.98	88.5
5	3.04	1.41	99.9	23	1.22	1.61	94.1
6	2.92	1.65	100.	24.	2.31	1.50	87.2
7	0.967	2.07	99.2	25	1.93	1.65	93.9
8	0.767	2.33	96.4	26	1.64	1.79	97.6
9	3.11	2.05	99.9	27	2.78	2.42	96.6
11	2.92	2.33	99.9	28	1.84	2.16	87.6
12	2.84	2.53	99.9	29	1.61	2.33	80.8
13	3.54	1.94	99.8	30	2.61	2.71	98.2
14	3.40	2.00	99.6	31	2.58	3.05	100.
15	3.22	2.17	99.8	32	2.78	1.62	99.2
16	3.02	2.31	99.8	33	2.71	1.89	99.4
17	1.15	3.28	94.1	34	2.46	1.96	98.4
18	1.19	3.44	94.9	35	2.61	2.41	99.6

Table V. Comparison of Steric Effects upon Acidic and Basic Catalyzed Hydrolysis

Set	Solvent	T, °C	ψ_A
	Acidic		
7	62% w/w MeAc–H_2O	30.1	−0.967
23	75% v/v MeAc–H_2O	35	−1.22
	Basic		
			ψ_B
6	62% w/w MeAc–H_2O	20	−2.92
11	70% v/v MeAc–H_2O	35	−2.92

as the υ_X and υ_{CH_2X} values. We may now obtain the defining equation for υ_{OX} values from set 10.

$$\upsilon_{OX} = -0.329 \log k_{OX} + 0.701 \qquad (9)$$

Values of υ_{OX} obtained from set 10, and from other sets, are set forth in Table III. Data for the remaining 34 sets were then correlated with the equation

$$\log k_{OX} = \psi \upsilon_{OX} + h \qquad (10)$$

Values of ψ, h, and $100r^2$ (which represents the percent of the data accounted for by the correlation) are reported in Table IV. For other statistics, see the paragraph at the end of this paper. All the 34 sets gave significant correlations.

The correlations obtained for sets 7, 8, 23, and 24 suggest that in these sets involving acid-catalyzed hydrolysis of alkyl acetates the compounds in the set are reacting by the same mechanism. If this were not the case, excellent correlations would not be obtained.

To verify eq 7, we have correlated υ_{OX} with υ_{CH_2X} by means of the equation

$$\upsilon_{OX} = m\upsilon_{CH_2X} + c \qquad (11)$$

The results are: m, 0.959; c, −0.100; r, 0.967; F, 159.1 (99.9% CL); s_{est}, 0.0562; s_m, 0.0760 (99.9% CL); s_c, 0.0627 (80.0% CL); n, 13. As is predicted by eq 7, m is not significantly different from 1. We conclude that eq 7 is verified.

It is of interest to compare the magnitude of the steric effect upon the basic hydrolysis of alkyl acetates with that upon the acidic hydrolysis. This may be done by comparing ψ values under reaction conditions which are as similar as possible. Such comparisons are made in Tables V and VI. The results show clearly that acid-catalyzed hydrolysis exhibits a much smaller steric effect than basc-catalyzed hydrolysis. The ψ values of sets 4, 5, and 6 show that the dependence of ψ on temperature is slight. Thus, comparison between sets 6 and 7 is justified. It is unlikely that the difference in solvent between sets 23 and 11 would interfere with comparison between values for these sets. The large difference between ψ_A and ψ_B found for hydrolysis of RCO_2X contrasts with the much smaller difference found for hydrolysis of XCO_2R (X is variable, R is constant). If we compare values of ψ for the hydrolysis of RCO_2X with ψ values for other carbonyl reactions as is done in Table VI, we observe that the ψ values for basic ester hydrolysis of alkyl acetates and ethyl carboxylates are about 0.35 unit apart in 70% v/v MeAc–H_2O, whereas the ψ values for acid hydrolysis in this medium differ by 0.76. The greater difference in ψ for alkyl acetate hydrolyses as compared with ethyl carboxylate hydrolyses is then largely due to the comparatively small value of ψ for the acid hydrolyses of alkyl acetates.

Comparing ψ values for basic hydrolysis of alkyl formates and acetates in water, the alkyl formates have a much smaller value in accord with the fact that the tetrahedral intermediate for their hydrolysis has a constant H atom, whereas that for the hydrolysis of alkyl acetates has a constant Me group. The ψ value for the basic hydrolysis of the amides is between that for the acetates and that for the formates. This is in accord

Table VI. Comparison of ψ Values under Similar Reaction Conditions

Substrate	Reagent	Solvent	T, °C	ψ	Source
MeC(=O)OX	H_3O^+	75% v/v MeAc–H_2O	35	−1.22	*a*
XC(=O)OEt	H_3O^+	70% v/v MeAc–H_2O	35	−1.98	*b*
MeC(=O)OX	OH^-	70% v/v MeAc–H_2O	35	−2.92	*c*
XC(=O)OEt	OH^-	70% v/v MeAc–H_2O	35	−2.57	*d*
MeC(=O)OX	OH^-	H_2O	30.0	−2.61	*e*
HC(=O)OX	OH^-	H_2O	35	−1.40	*f*
XC(=O)NH_2	OH^-	H_2O	75	−1.87	*g*

[a] This work, set 23. [b] Reference 3, set 8. [c] This work, set 11. [d] Reference 4, set 2. [e] This work, set 35. [f] This work, set 20. [g] Reference 8, set 7.

with its tetrahedral intermediate, which has a constant NH_2 group.

A comparison of ψ values for sets 3, 11, 31, and 35 shows that the effect of solvent on the ψ value for the basic hydrolysis of alkyl acetates is small.

At the suggestion of a referee, we have examined the correlation of data for the alkaline hydrolysis of ZCO_2X in 40% aqueous dioxane at 35 °C with the equation

$$\log k = \psi_1 \upsilon_Z + \psi_2 \upsilon_{OX} + h \qquad (12)$$

The data used were a combination of set 3 from Table I and set 5 from ref 4. The results of the correlation with eq 12 are: multiple correlation coefficient, 0.995; F test for significance of regression, 64.30 (99.9% CL); s_{est}, 0.0609; s_{ψ_1}, 0.0805 (99.9% CL); s_{ψ_2}, 0.0741 (00.0% CL); s_h, 0.0822 (99.9% CL); partial correlation coefficient of υ_Z on υ_{OX}, 0.479 (90.0% CL); ψ_1, −2.06; ψ_2, −2.54; h, 3.23; number of points in set, 15; range in $\log k$, 2.27. Thus, the rates of hydrolysis of esters substituted in both the acyl and alkoxy moieties can be successfully treated by means of eq 12.

The success of this work in evaluating υ_{OX} constants which are on the same scale as, and can therefore be used in the same correlation as, υ constants for alkyl, halogen, haloalkyl, oxyalkyl, and other groups is not yet completely established. We hope to demonstrate in future work that the υ_{OX} values reported here are indeed applicable to data sets containing a mixture of substituent types.

Supplementary Material Available: the results of the correlations with eq 7 and 8 and values of σ_I and σ_R for OR groups and complete statistics for the correlations of the data in Table I with eq 10 (5 pages). Ordering information is given on any current masthead page.

Registry No.—Acetic acid, 64-19-7; 4-nitrobenzoyl chloride, 122-04-3.

References and Notes

(1) R. W. Taft, *J. Am. Chem. Soc.*, **74,** 3120 (1952).
(2) R. W. Taft in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 644–645.
(3) M. Charton, *J. Am. Chem. Soc.*, **97,** 1552 (1975).
(4) M. Charton, *J. Am. Chem. Soc.*, **97,** 3691 (1975).
(5) M. Charton, *J. Am. Chem. Soc.*, **97,** 3694 (1975).
(6) M. Charton, *J. Am. Chem. Soc.*, **97,** 6159 (1975).
(7) M. Charton and B. I. Charton, *J. Am. Chem. Soc.*, **97,** 6472 (1975).
(8) M. Charton, *J. Org. Chem.*, **41,** 2217 (1976).
(9) M. Charton, *J. Org. Chem.*, **41,** 2906 (1976).
(10) M. Charton, *J. Org. Chem.*, **42,** 2528 (1977).

Steric Effects. 10. Substituents at Nitrogen in Carbonyl Compounds

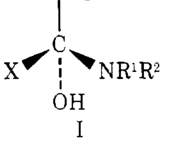
Marvin Charton

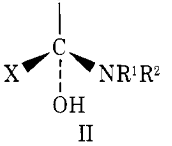
Department of Chemistry, Pratt Institute, Brooklyn, New York 11205

Received January 20, 1976

Twelve sets of carbonyl addition reactions including rate constants for acidic and basic hydrolysis of N-substituted amides, rate constants for the reaction of methyl acetate with alkylamines, and rate constants for the reaction of piperonal with alkylamines were correlated with the modified Taft equation using $\upsilon_{CHX^1X^2}$ constants; 16 sets of data were correlated with $\upsilon_{NX^1X^2}$ constants. Very good results were obtained. The $\upsilon_{NX^1X^2}$ constants were defined in this work. Eighteen values of $\upsilon_{NX^{12}}$ are given. The results verify the validity and generality of the equation $\upsilon_{Z_1X^1X^2} = \upsilon_{Z_2X^1X^2} + c$. The variation of ψ with structure is discussed for a variety of acid-catalyzed and base-catalyzed hydrolyses of carbonyl derivatives.

In the preceding paper of this series,[1] steric substituent constants were developed for alkoxy groups. These constants were applicable to addition reactions of carbonyl compounds. In this work we consider the application of the techniques we have developed to the definition of steric substituent constants for alkylamino and dialkylamino substituents. Let us consider substituent effects upon rates of acid and alkaline hydrolysis of N-substituted amides. The tetrahedral intermediates involved in the acid and alkaline hydrolysis are I and II, respectively. The X group represents a constant substituent; the NR^1R^2 group varies. We have shown that the electrical effects of alkyl groups in base-catalyzed ester hydrolysis reactions are constant,[2] as are electrical effects of alkoxy groups.[1] It seems likely that the electrical effects of alkylamino and dialkylamino groups are also constant in addition reactions of the carbonyl group. In support of this contention, the σ_m and σ_p substituent constants of NHX groups are given by the equations[3]


I


II

$$\sigma_{m\text{-NHX}} = 1.11\, \sigma_{m\text{-X}} - 0.187 \qquad (1)$$

$$\sigma_{p\text{-NHX}} = 1.33\, \sigma_{m\text{-X}} - 0.476 \qquad (2)$$

According to Taft

$$\sigma_{INHX} = (3\, \sigma_{m\text{-NHX}} - \sigma_{p\text{-NHX}})/2 \qquad (3)$$

and

$$\sigma_{RNHX} = \sigma_{p\text{-NHX}} - \sigma_{INHX} \qquad (4)$$

From eq 1, 2, and 3

$$\sigma_{INHX} = (3.33\, \sigma_{m\text{-X}} - 0.561 - 1.33\sigma_{m\text{-X}} + 0.476)/2 \qquad (5)$$

$$= (2\sigma_{m=X} - 0.085)/2 = \sigma_{m\text{-X}} - 0.043 \qquad (6)$$

Now, according to Taft,[4]

$$\sigma_{m\text{-X}} = \sigma_{IX} + \sigma_{RX}/3 \qquad (7)$$

We are interested in the case in which X is alkyl. For values of σ_I and σ_R for alkyl groups, see the paragraph at the end of this paper. The average value of σ_I is −0.01 ± 0.02. Since the error in the σ_I values is probably 0.05, we conclude that σ_I values for alkyl groups are constant. Examination of the σ_R values for alkyl groups shows that they average 0.16 ± 0.03; the error in σ_R is not less than 0.05; therefore these values are again constant. Then from eq 7, σ_m for alkyl groups is con-