consistent with structure IVa as are the ultraviolet and visible spectra.[17]

(2) The same product, IVa, was obtained in 85% yield when II was treated with anhydrous hydrogen fluoride at room temperature.

B. From 7-(2-Carboxyphenyl)benz[*a*]anthracene (III).—The same product, IVa, was obtained in 91% yield when III was treated with anhydrous hydrogen fluoride at room temperature.

Trinitrofluorenone Adduct of Dibenzo[*hi,l*]chrysen-9-one.—A hot solution of 0.048 g. of trinitrofluorenone in 15 ml. of ethanol was added to a hot solution of 0.050 g. of dibenzo[*hi,l*]chrysen-9-one in 15 ml. of benzene. On cooling, deep red crystals formed. Recrystallization from benzene–ethanol gave fine red needles, m.p. 201.5–202°.

Anal. Calcd. for $C_{38}H_{19}N_3O_8$: C, 70.69; H, 2.97; N, 6.51. Found: C, 70.73; H, 2.69; N, 6.35.

9H-Dibenzo[*hi,l*]chrysene.—A solution of 0.2 g. (0.0006 mole) of IVa and 0.081 g. (0.0006 mole) of aluminum chloride in 25 ml. of benzene was added slowly to a warm slurry of 0.029 g. (0.0008 mole) of lithium aluminum hydride and 0.100 g. (0.0008 mole) of aluminum chloride in 4 ml. of dry ether. After 20 min., the mixture was decomposed with 3 ml. of 6 *N* sulfuric acid and worked up in the usual way. The desired product, 0.11 g. (58%), was obtained as fine orange needles, m.p. 157–158°. Its infrared spectrum, in contrast to the spectrum of IVa, showed the absence of a carbonyl band at 1650 cm.$^{-1}$ and the appearance of the band for aliphatic carbon–hydrogen linkages at 2900 cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.90; H, 5.10. Found: C, 94.62; H, 5.31.

Acknowledgment.—We wish to thank Dr. John D. Vaughan for constructive suggestions regarding the electron localization energies and frontier electron density correlations. This investigation was supported in part by Research Grant No. CY-4412(C2) from the National Institutes of Health, U. S. Public Health Service.

Definition of "Inductive" Substituent Constants

MARVIN CHARTON

Department of Chemistry, School of Engineering and Science, Pratt Institute, Brooklyn, New York

Received October 23, 1963

The definition of σ_I constants may conveniently be made by means of the equation $\sigma_{I,X} = m(pK_{a,X}) + c$, where $pK_{a,X}$ is that of a substituted acetic acid in water. In general, no steric effects are observed. Ionization constants of 2- or 3-substituted propanoic acids, substituted methylamines, 2-substituted ethylamines, and substituted methyl phosphonic acids in water and of acetic acids in 80% Methyl Cellosolve–water have also been examined as secondary reference series for the definition of σ_I constants. Data available in the literature have permitted the definition of more than 100 σ_I values.

The Hammett equation has been used extensively for the correlation of rate and equilibrium data and of certain physical properties with substituent effects. In its most general form the Hammett equation may be written

$$Q_X = \rho\sigma_X + Q_H \qquad (1)$$

where Q is the quantity correlated, σ is a constant representing the electrical effect of the X substituent, ρ is the slope, and Q_H is the intercept. The nature of the substituent constant σ_X appears to depend upon the hybridization state of the carbon atom to which the substituent is bonded. The electrical effect of a substituent X bonded to an sp^3 hybridized carbon atom is best represented by the σ_I constants.[1] These constants were originally defined by Taft[1a] from the equation

$$\sigma_I = \left[\log\left(\frac{k}{k^0}\right)_{OH^-} - \log\left(\frac{k}{k^0}\right)_{H^+}\right]/6.23 \qquad (2)$$

where OH^- and H^+ denote the base- and acid-catalyzed hydrolyses of esters, and k and k^0 are the rates of reaction of the substituted and unsubstituted compounds, respectively. This definition is inconvenient in that it requires two measurements to define a new value of σ_I, and also suffers from the difficulty of obtaining reliable and reproducible rate measurements in different laboratories. The choice of this approach to the definition of σ_I values by Taft[1b] was due to an attempt to eliminate steric effects. The steric effect in both acid- and base-catalyzed hydrolyses of esters is believed to be the same, as the transition states proposed for these reactions differ only by a proton, and of course the steric requirements for a proton must be quite small.

Our need for a convenient source of new σ_I values has led us to consider the alternative definition of σ_I constants in terms of the equation

$$\sigma_{I,X} = b(pK_{a,X}) + d \qquad (3)$$

where b is the slope of the regression line which minimizes deviation on the pK_a values and d is the intercept of this line and where the σ_I values are defined in terms of the pK_a values of the corresponding substituted acetic acids. There is nothing new in this proposal; that substituent effects are "inductive" in nature has been suggested many times before.[2] Taft's definition is based on the assumption that in addition to the polar effects of a substituent in an aliphatic compound there is also a significant steric effect which must be accounted for. If this steric effect is not significant (or, at most, rarely significant), then eq. 3 constitutes a more convenient definition. The advantages of such a definition are threefold. First, only one measurement suffices to define a new value of σ_I; second, the pK_a values may be more reliably and reproducibly determined; third, the definition of σ_I values would now be directly comparable to that of the Hammett[3a,b] substituent constants.

To determine whether such a definition is justifiable, pK_a values of substituted acetic acids in water at 18 and at 25° generally taken from the compendium of

---

(1) (a) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); (b) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960); (c) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).

(2) G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 217.

(3) (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940; (b) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (c) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.

TABLE I

DATA USED IN CORRELATIONS[a-c]

Series	Temp., °C.	$K \times 10^5$ (X)
1a	5	1.700 (H), 1.305 (Me), 1.574 (Et), 20.82 (AcNH), 18.69 (EtCONH), 12.28 (H_2NCONH), 359.20 (CN),[d] 28.97 (MeO)
1b	10	1.729 (H), 1.326 (Me), 1.576 (Et), 21.09 (AcNH), 18.95 (EtCONH), 12.60 (H_2NCONH), 357.45 (CN),[d] 28.58 (MeO)[e]
1c	15	1.745 (H), 1.336 (Me), 1.569 (Et), 278.9 (F), 143.0 (Cl), 133.31 (Br), 71.90 (I), 21.25 (AcNH), 19.13 (EtCONH), 12.90 (H_2NCONH), 352.93 (CN),[d] 28.15 (MeO)[e]
1d	18	1.734 (H), 1.32 (Me), 1.53 (Et), 129 (Br), 70 (I), 14.6 (OH)
1e	20	1.753 (H), 1.338 (Me), 1.592 (Et), 268.4 (F), 139.4 (Cl), 129.63 (Br), 69.46 (I), 22.02 (AcNH), 19.21 (EtCONH), 13.22 (H_2NCONH), 346.94 (CN),[d] 27.60 (MeO)[e]
1f	25	1.754 (H), 1.336 (Me), 1.515 (Et), 259.6 (F), 135.9 (Cl), 125.30 (Br), 66.80 (I), 338.76 (CN),[d] 4.927 (Ph),[f] 2.166 ($PhCH_2$),[f] 14.76 (OH), 26.89 (MeO),[d] 21.39 (AcNH)
1g	30	1.750 (H), 1.326 (Me), 1.484 (Et), 249.0 (F), 130.79 (Cl), 120.78 (Br), 64.06 (I), 329.78 (CN),[d] 21.23 (AcNH), 19.02 (EtCONH), 13.38 (H_2NCONH), 26.10 (MeO)[e]
1h	35	1.728 (H), 1.310 (Me), 1.439 (Et), 237.9 (F), 125.94 (Cl), 115. 88 (Br), 61.26 (I), 319.52 (CN),[d] 20.99 (AcNH), 18.82 (EtCONH), 13.39 (H_2NCONH), 25.14 (MeO)[e]
1i	40	1.703 (H), 1.284 (Me), 1.395 (Et), 20.68 (AcNH), 18.58 (EtCONH), 13.33 (H_2NCONH), 308.51 (CN),[d] 24.40 (MeO)[e]
1j	45	1.670 (H), 1.257 (Me), 1.347 (Et), 20.21 (AcNH), 18.19 (EtCONH), 13.17 (H_2NCONH), 296.40 (CN),[d] 23.37 (MeO)[e]
1k	50	1.633 (H), 1.229 (Me), 1.302 (Et), 19.67 (AcNH), 17.77 (EtCONH), 12.95 (H_2NCONH), 14.16 (OH), 22.34 (MeO)[e]
2a	18	1.32 (H), 1.44 (Me), 1.56 (Et), 1.62 (Pr), 1.32 (Cl), 107 (Br), 78 (I), 13.8 (OH)
2b	25	1.336 (H), 1.42 (Me), 13.87 (OH), 19.27 (AcNH), 12.81 (H_2NCONH)
3a	18	1.32 (H), 1.53 (Me), 1.51 (Et), 1.43 (P), 1.456 (*i*-Pr), 1.63 (*t*-Bu), 8.0 (Cl), 10.2 (Br), 8.2 (I), 2.0 (C_2H_3)
3b	25	1.336 (H), 1.515 (Me), 1.44 (Et), 2.166 (Ph), 3.588 (AcNH), 3.256 (H_2NCONH)
		pK_a[g] (X)
4	25	7.33 (*i*-Pr), 7.30 $H(CH_2)_6$, 5.78 (OH), 5.04 (Cl), 6.73 (Ph)
5	25	10.624 (H),[h] 10.631 (Me),[h] 10.568 (Et),[h] 10.640 (Pr),[h] 9.49 (CH_2CH_3),[i] 9.37 (Ph),[j] 9.830 ($PhCH_2$),[j] 5.34 (CN),[k] 7.93 ($CONH_2$)[l]
6	25	10.631 (H),[h] 10.568 (Me),[h] 10.640 (Et),[h] 9.830 (Ph),[j] 9.498 (OH),[h] 9.20 (OMe),[m] 10.20 ($PhCH_2$)[j]
7[n]	25	2.38 (H), 2.43 (Me), 2.49 (Et), 1.40 (Cl), 1.14 (Br), 1.30 (I), 1.91 (OH), 1.85 (Ph)
8[o]	25	7.74 (H), 8.05 (Me), 8.18 (Et), 6.30 (Cl), 6.52 (Br), 6.72 (I), 7.15 (OH), 7.4 (Ph)

[a] All data in water unless otherwise noted. [b] All data from ref. 4 unless otherwise noted; values chosen are those given by ref. 4 as very reliable or reliable; [c] Series 1a–k are substituted acetic acids, series 2a and b are 2-substituted propanoic acids, series 3a and b are 3-substituted propanoic acids. [d] F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 2798 (1956). [e] E. J. King, *J. Am. Chem. Soc.*, **82,** 3575 (1960). [f] E. J. King and J. E. Prue, *J. Chem. Soc.*, 275 (1961). [g] W. Simon, G. H. Lyssy, A. Morikofer, and E. Heilbronner, "Zusammenstellung von scheinbaren Dissoziations Konstanten im Losungsmittelsystem Methylcellosolve–Wasser," Vol. I, Juris-Verlag, Zurich, 1959; P. F. Sommer and W. Simon, *ibid.*, Vol. II, 1961. [h] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 65. [i] G. Girault-Vexlearschi, *Bull. soc. chim. France*, 589 (1956). [j] W. H. Carothers, C. F. Bickford, and G. J. Hurwitz, *J. Am. Chem. Soc.*, **49,** 2908 (1927). [k] G. W. Stevenson and D. Williamson, *ibid.*, **80,** 5943 (1958). [l] M. Zieff and J. T. Edsall, *ibid.*, **59,** 2245 (1937). [m] R. J. Bruehlman and F. H. Verhoek, *ibid.*, **70,** 1407 (1948). [n] pK_{a_1} value. [o] pK_{a_2} value.

Kortum, Vogel, and Andrussow[4] were correlated with the σ_I values given by Taft.[1b] From the series at 25°, σ_I constants were calculated for the EtCONH and H_2NCONH groups (these values are reported in Table II). These constants were then used in conjunction with those of Taft to correlate pK_a values of substituted acetic acids at other temperatures ranging from 5 to 50°. The pK_a values in water at temperatures from 5 to 50° in 5° intervals were considered by Kortum, *et al.*, to be very reliable while those at 18° were considered reliable.

The pK_a values used in the correlation are given in Table I. The values of σ_I which were accepted as standard and used in the correlations are given in Table II.

TABLE II

PRIMARY σ_I VALUES

X	σ_I	X	σ_I	X	σ_I
Et	−0.05	F	0.52	OH	0.25
Me	−0.05	Cl	0.47	MeO	0.25
H	0.00	Br	0.45	NHAc	0.28
$PhCH_2$	0.04	I	0.39	CN	0.58
Ph	0.10	*t*-Bu	−0.07	EtCONH	0.25[a]
				H_2NCONH	0.21[a]

[a] From Table V.

Results

The results of the correlations are given in Table III together with values of b and d for use in eq. 3. The

TABLE III

RESULTS OF CORRELATIONS

Series	ρ	r[a]	s[b]	Q_H	b	d	n[c]
1a	−3.869	0.994	0.0940	4.681	−0.2556	1.213	8
1b	−3.860	0.995	0.0892	4.676	−0.2565	1.214	8
1c	−3.938	0.997	0.0733	4.678	−0.2523	1.191	12
1d	−3.905	0.997	0.0809	4.700	−0.2544	1.197	6
1e	−3.917	0.997	0.0671	4.676	−0.2539	1.189	12
1f	−3.950	0.996	0.0806	4.712	−0.2512	1.186	13
1g	−3.875	0.998	0.0618	4.682	−0.2568	1.204	12
1h	−3.857	0.998	0.0588	4.688	−0.2582	1.217	12
1i	−3.816	0.997	0.0676	4.693	−0.2605	1.231	8
1j	−3.808	0.997	0.0652	4.703	−0.2611	1.236	8
1k	−3.843	0.994	0.0699	4.726	−0.2568	1.233	8
2a	−3.871	0.994	0.105	4.709	−0.2554	1.205	8
2b	−3.732	0.988	0.100	4.753	−0.2618	1.247	5
3a	−1.607	0.982	0.0734	4.776	−0.6003	2.981	10
3b	−1.306	0.972	0.0490	4.796	−0.7241	3.477	6
4	−4.646	0.993	0.132	7.13	−0.2124	1.517	5
5	−8.570	0.997	0.156	10.29	−0.1159	1.192	9
6	−4.388	0.970	0.155	10.42	−0.2145	2.239	7
7	−2.325	0.962	0.160	2.32	−0.3979	0.9630	8
8	−3.125	0.987	0.121	7.87	−0.3120	2.459	8

[a] Correlation coefficient. [b] Standard deviation. [c] Number of points in series.

---

(4) G. Kortum, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, **1,** 190 (1961).

TABLE IV

CALCULATED σ_I VALUES

X	pK_a^{a}	σ_I^{b}	Series^{c}	X	pK_a^{a}	σ_I^{b}	Series^{c}
CH_2Cl	4.10	0.15	1d	CH_2Br	3.991	0.18	1d
CH_2I	4.086	0.16	1d	EtO	3.652	0.27	1d
Me_2COHCH_2	4.873	−0.04	1d	$MeCHOHCH_2$	4.686	−0.01	1d
$PhCH_2SCH_2$	4.463	0.06	1d	$PhCH_2CH_2S$	3.7945	0.23	1d
PhCHOH	4.40	0.08	1d	$C_2H_3CH_2$	4.70	0.00	1d
i-Pr	4.770	−0.02	1d	Pr	4.821	−0.03	1d
Bu	4.845	−0.04	1d	*i*-Bu	4.8368	−0.03	1d
s-Bu	4.836	−0.03	1d	*t*-$BuCH_2$	4.788	−0.02	1d
i-Pr	4.8348	−0.04	1e	Pr	4.7673	−0.02	1e
EtO_2CNH	3.66	0.26	1e	HCONH	3.43	0.32	1e
CCl_3CH_2	4.21^{d}	0.12	1e	$CCl_3CH_2CH_2$	4.52^{d}	0.04	1e
$Cl_2C{=}CH$	4.04^{d}	0.16	1e	$Cl_2C{=}CHCH_2$	4.57^{d}	0.03	1e
CO_2^-	5.39513^{d}	−0.17	1f	EtCONH	3.7176	0.25	1f
H_2NCONH	3.8758	0.21	1f	$AcNHCH_2$	4.4452	0.07	1f
C_2H_3	4.3521	0.09	1f	H_2NCO	3.6413	0.27	1f
H_2NCOCH_2	4.5388	0.05	1f	$C_2H_3CH_2$	4.6747	0.01	1f
PhO	3.171	0.39	1f	1-$C_{10}H_7$	4.2362	0.12	1f
2-$C_{10}H_7$	4.259	0.12	1f	HC_2	3.32^{g}	0.35	1f
HC_2CH_2	4.21^{g}	0.13	1f	SO_3^-	4.20^{h}	0.13	1f
SH	3.68^{i}	0.26	1f	NO_2	1.68^{i}	0.76	1f
$MeSO_2$	2.36^{i}	0.59	1f	PhS	3.52^{i}	0.30	1f
MeS	3.72^{i}	0.25	1f	EtS	3.74^{i}	0.25	1f
i-PrS	3.72^{i}	0.25	1f	PrS	3.77^{i}	0.24	1f
BuS	3.91^{i}	0.23	1f	Ph_3CS	4.30^{i}	0.11	1f
$PhCH_2S$	3.73^{i}	0.25	1f	Bu	4.857	−0.03	1f
i-Bu	4.845	−0.03	1f	*t*-Bu	4.998^{j}	−0.07	1f
$MeCH{=}CH{-}$	4.507	0.05	1f	$EtCH{=}CH$	4.516	0.05	1f
$MeCH{=}CHCH_2$	4.719	0.00	1f	$Me_2C{=}CH$	4.600	0.03	1f
$BuCH_2$	4.893	−0.04	1f	$BuCH_2CH_2$	4.8945	−0.04	1f
$Bu(CH_2)_3$	4.959	−0.06	1f	cy-C_6H_{11}	4.801	−0.02	1f
CF_3	3.063	0.42	1f	cy-C_5H_9O	3.699	0.26	1f
cy-$C_6H_{11}O$	3.538	0.30	1f	cy-$C_6H_{11}S$	3.488	0.31	1f
cy-$C_6H_{11}Se$	3.187	0.38	1f	Me_3Si	5.22	−0.13	1f
Me_3SiCH_2	4.907	−0.05	1f	$PhMe_2Si$	5.27	−0.14	1f
AsO_3H^-	4.670	0.01	1f	ONO_2	2.26^{k}	0.62	1f
Me_3N^+	1.83^{i}	0.73	1f	EtO_2C	3.35^{i}	0.34	1f
MeO_2C	3.35^{l}	0.34	1f	$PhSO_2$	2.44^{i}	0.57	1f
PhSO	2.66^{i}	0.52	1f	SCN	2.523^{m}	0.58	1f
N_3	3.03	0.42	1f	PrO	3.65^{i}	0.27	1f
BuO	3.66^{i}	0.27	1f	*s*-BuO	3.67^{i}	0.26	1f
i-PrO	3.69^{i}	0.26	1f	CO_2H	$3.14764^{f,n}$	0.39	1f
CH_2CN	3.991	0.18	1f	CH_2CF_3	4.156	0.14	1f
$CH_2C_3F_7$	4.18	0.14	1f	$SiMe_2OSiMe_3$	5.22	−0.13	1f
3-Indolyl	4.75^{o}	−0.01	1f	2-Thienyl	3.89^{p}	0.21	1f
BzNH	3.66^{q}	0.27	1f	Ac	3.58	0.29	1f
PhNHCO	3.717^{m}	0.25	1f	$PhNHCOCH_2$	4.701^{m}	0.00	1f
CH_2OH	4.507^{m}	0.05	1f	CH_2OMe	4.461^{r}	0.07	1f
$PhCH_2CH_2$	4.757	−0.01	1f	$Me_2C{=}NO$	3.56^{s}	0.29	1f
CH_2CO_2Me	4.029^{t}	0.17	1f	$PhSO_2NH$	3.461^{u}	0.32	1f
CH_2SH	4.32^{v}	0.10	1f	$Me_3Si(CH_2)_2$	4.886	−0.04	1f
$MeSi(CH_2)_3$	4.963	−0.06	1f	$H_2NCO(CH_2)_2$	4.600	0.03	1f
$H_2NCO(CH_2)_3$	4.629	0.02	1f	cy-$C_6H_{11}CH_2O$	3.903	0.21	1f
cy-$C_6H_{11}CH_2$	4.910	−0.05	1f	cy-$C_6H_{11}(CH_2)_4$	4.951	−0.06	1f
Me_2NH^+	1.95	0.70	1f	$MeNH_2^+$	2.35	0.60	1f
NH_3^+	2.3503	0.60	1f	$EtNH_2^+$	2.34	0.60	1f
$PrNH_2^+$	2.35	0.60	1f	$BuNH_2^+$	2.35	0.60	1f
i-$BuNH_2^+$	2.35	0.60	1f	H_3NO^+	2.87^{s}	0.47	1f
PhNAc	3.914^{m}	0.22	1f	Pr	4.8511	−0.04	1g
i-Pr	4.7945	−0.03	1g	MeCHOH	4.648	0.02	2a
SeCN	2.551^{w}	0.58	2b	SCN	2.441^{x}	0.61	2b
$SCONH_2$	3.487^{x}	0.33	2b	SO_2Me	2.44	0.61	2b
SO_2Et	2.448	0.60	2b	SO_2Pr	2.507	0.59	2b
SO_2-*i*-Pr	2.522	0.59	2b	cy-$C_6H_{11}O$	3.638	0.29	2b
1-$C_{10}H_7NAc$	3.693^{m}	0.26	2b	2-$C_{10}H_7NAc$	3.627^{m}	0.27	2b
2-Furyl	6.97^{y}	0.04	4	2-Thienyl	6.43	0.15	4
2-Thienylmethyl	6.91^{y}	0.05	4	3-Indolyl	7.14^{y}	0.00	4
				1-$C_{10}H_7CH_2$	6.81^{y}	0.07	4
CF_2H	7.52^{i}	0.32	5	$Ph(CH_2)_2$	10.201^{z}	0.01	5

TABLE IV (*Continued*)

X	pK_a[a]	σ_I[b]	Series[c]	X	pK_a[a]	σ_I[b]	Series[c]
CO_2^-	9.7796	0.06	5	$CH_2CO_2^-$	10.2350	0.01	5
$CH_2NH_3^+$	7.149[aa,f]	0.36	5	CH_2NH_2	9.627[aa,e]	0.08	5
$Ph(CH_2)_3$	10.394[z]	−0.01	5	$Ph(CH_2)_4$	10.486[z]	−0.02	5
cy-C_6H_{11}	10.49[bb]	−0.02	5	HC_2	8.15[bb]	0.25	5
PhCHMe	9.80[bb]	0.06	5	$H(CH_2)_7$	10.57[bb]	0.03	5
t-Bu	10.24[bb]	0.01	5	CH_2OH	9.498[aa]	0.09	5
CO_2Me	7.66[cc]	0.30	5	CH_2CO_2Et	9.13[cc]	0.13	5

[a] All data in water; all pK_a values from ref. 4 unless otherwise noted. [b] σ_I values in which the hundredths place is upper case are calculated from reliable thermodynamic pK_a values using those series in Table III for which correlation is significant at the 99.9% confidence level. [c] Series from which σ_I was calculated; numbers refer to Table I. [d] A. N. Nesmeyanov, L. I. Zakharkin, and R. K. Friedlina, *Izv. Akad. Nauk. SSSR, Otdel. Khim. Nauk.*, 40 (1955). [e] Includes statistical factor 2. [f] Includes a statistical factor of 0.5. [g] G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4761 (1956). [h] R. P. Bell and G. A. Wright, *Trans. Faraday Soc.*, **57**, 1377 (1961). [i] H. C. Brown, D. H. McDaniel, and O. Hafliger, "Determination of Organic Structures by Physical Methods," Vol. 1, Academic Press, New York, N. Y., 1955. [j] L. Otros, F. Sirokman, and O. Gall, *Univ. Szegediensis Acta Phys. Chem.*, [N.S.]**4**, 131 (1958). [k] K. S. McCallum and W. D. Emmons, *J. Org. Chem.*, **21**, 367 (1956). [l] W. D. Treadwell and E. Wettstein, *Helv. Chim. Acta*, **18**, 204 (1935). [m] W. Ostwald, *Z. physik. Chem.* (Leipzig), **3**, 241 (1889). [n] S. N. Das and D. J. G. Ives, *Proc. Chem. Soc.*, 373 (1961). [o] P. E. Pilet and M. A. Athanasiades-Mercantori, *Phyton Ann. rei Botan.*, **8**, 210 (1959). [p] E. Imoto and R. Motoyama, *Bull. Naniwa Univ.*, **2A**, 127 (1954). [q] E. Larrson, *Z. anorg. Chem.*, **155**, 247 (1926). [r] M. H. Palomaa, *Ann. Acad. Sci. Fennicae*, [A]**3**, 15 (1912). [s] E. Borek and H. T. Clarke, *J. Biol. Chem.*, **125**, 483 (1938). [t] J. Walker, *J. Chem. Soc.*, **61**, 705 (1892). [u] J. M. Loven, *Z. Physik. Chem.* (Leipzig), **19**, 456 (1896). [v] H. Borsook, E. L. Ellis, and H. M. Huffman, *J. Biol. Chem.*, **117**, 281 (1937). [w] A. Fredga, *J. prakt. Chem.*, [2]**123**, 129 (1929). [x] A. Fredga, *ibid.*, [2]**123**, 110 (1929). [y] In 80% Methyl Cellosolve–water; see footnote. *g*, Table I. [z] Footnote *j*, Table I. [aa] Footnote *h*, Table I. [bb] Footnote *i*, Table I. [cc] J. T. Edsall and M. H. Blanchard, *J. Am. Chem. Soc.*, **55**, 2337 (1933).

values of *b* and *d* permit the calculation of new σ_I constants.

As is shown by the correlation coefficients (r) and the standard deviations (s), the correlations are excellent. The success of these correlations demonstrates the absence of any steric effect. The results obtained are possible only if any steric effect which existed were constant throughout the series. A glance at the substituents involved in the series correlated suffices to show enormous variation in bulk and shape. Under these circumstances no constant steric effect is possible. Thus no steric effect whatsoever seems to be present in these series. The results justify definition of σ_I constants by eq. 3. A number of σ_I constants have been calculated from pK_a values extant in the literature. The pK_a values used and the σ_I values obtained are given in Table IV. Preferred values of the σ_I constants are given in Table V. Comparisons have been made with values given by Taft or values obtained from these equations.

$$\sigma_I = [(3\sigma_m - \sigma_p)/2] \quad (4)$$

$$\sigma_I = \sigma^*/6.23 \quad (5)$$

In general, the agreement is good, when comparison is made with the values obtained from eq. 4 and 5 or those quoted by Taft for reactivities in weakly protonic solvents. The values obtained by Taft and co-workers[1c] from F^{19} shielding parameters in weakly protonic solvents show fair agreement. In order more effectively to compare these $\sigma_{I,F^{19}}$ values with the σ_{I,pK_a} values in Table V, we have correlated the latter with the former (slope = 0.77, intercept = 0.08, r = 0.953, s = 0.07, n = 17). There is apparently a difference in scale between the two sets of σ_I values.

Supplementary Series for the Definition of σ_I.—We have examined the possibility of using series other than substituted acetic acids in water as a means of obtaining σ_I values. The series studied include ionization constants of 2-substituted propanoic acids in water at 18 (series 2a) and 25° (series 2b); 3-substituted propanoic acids in water at 18 (series 3a) and 25° (series 3b); substituted acetic acids in 80% Methyl Cellosolve–water at 25° (series 4); substituted methylamines in water at 25° (series 5); 2-substituted ethylamines in water at 25° (series 6); and the first and second ionization constants of substituted methylphosphonic acids in water at 25° (series 7 and 8, respectively). Correlations were made using the primary σ_I constants given in Table II and in some cases σ_I constants from Table V which are believed accurate to the hundredth place. Among the requirements that a series must meet to be useful in the determination of σ_I values is that ρ have a large value; thus the series will reflect small differences in substituent effect. By this criterion, series 2a, 2b, 4–6, and 8 should be useful in the evaluation of σ_I constants. A more important criterion is a high level of correlation for the series. We have arbitrarily considered the 99.9% confidence level to represent the degree of correlation necessary for the definition of σ_I values, and the 99% confidence level for their estimation. Defined values are considered reliable in the hundredths place, estimated values are considered reliable in the tenths place. On this basis, of the supplementary series examined, series 2a and 5 may be used to define σ_I constants and all other supplementary series may be used to estimate σ_I values. Only those thermodynamic ionization constants considered by Kortum, Vogel, and Andrussow to be very reliable, together with more recent values obtained by the same careful techniques, were used to define σ_I constants.

Limitations of the Definition of σ from Eq. 3.—There is one obvious limitation on the method and that is the comparatively large error in measuring the pK_a values of fairly strong acids (pK_a less than 2). This problem is lessened by the fact that choice of one of the supplementary series will usually give a substituted acid in the range of conveniently measured pK_a.

Another more serious limitation is intramolecular hydrogen bonding between substituent and carboxyl group. Thus the thermodynamic functions of K_1 and K_2 for malonic acid have been interpreted as an indication of an intramolecular hydrogen bond. The value of K_1 does cause some decrease in correlation when the σ_I value of 0.30 suggested by Taft for the carboxyl group

TABLE V

PREFERRED σ_I VALUES

	This work	Reactivities	Taft F^{19} shielding	Eq. 4	Eq. 5
Alkyl and Cycloalkyl					
i-Pr	−0.03				−0.03
Pr	−0.03				−0.02
Bu	−0.04				−0.02
i-Bu	−0.03				−0.02
s-Bu	−0.03				−0.03
t-Bu	−0.07				
t-$\mathrm{BuCH_2}$	−0.02				−0.03
$\mathrm{BuCH_2}$	−0.04				
$\mathrm{Bu(CH_2)_2}$	−0.04				
$\mathrm{Bu(CH_2)_3}$	−0.06				
Cyclohexyl	−0.02				
Vinyl, Ethynyl, Aryl, and Heteroaryl					
$\mathrm{C_2H_3}$	0.09	0.05	0.01		
2,2-$\mathrm{MeC_2H}$	0.03				
trans-2-$\mathrm{Me_2C_2H_2}$	0.05			0.05	
trans-2-$\mathrm{EtC_2H_2}$	0.05				
$\mathrm{C_2H_3CH_2}$	0.00				
trans-2-$\mathrm{MeC_2H_2CH_2}$	0.00				−0.02
$\mathrm{HC_2}$	0.35				
$\mathrm{HC_2CH_2}$	0.13				
1-$\mathrm{C_{10}H_7}$	0.12				
2-$\mathrm{C_{10}H_7}$	0.12				
1-$\mathrm{C_{10}H_7CH_2}$	0.07				
$\mathrm{Ph(CH_2)_2}$	−0.01				
$\mathrm{Ph(CH_2)_2}$	−0.01				
$\mathrm{Ph(CH_2)_4}$	−0.02				
2-Thienyl	0.21				
2-Furyl	0.04				
3-Indolyl	−0.01				
2-Thienylmethyl	0.05				
Haloalkyl and Halovinyl					
$\mathrm{CF_3}$	0.42	0.41	0.41		0.37
$\mathrm{CF_3CH_2}$	0.14				
$\mathrm{C_3F_7CH_2}$	0.14				
$\mathrm{CCl_3CH_2}$	0.12				
$\mathrm{CCl_3(CH_2)_2}$	0.04				
$\mathrm{CF_2H}$	0.32				
$\mathrm{CH_2Cl}$	0.15	0.17	0.14		0.17
$\mathrm{CH_2Br}$	0.18				0.16
$\mathrm{CH_2I}$	0.16				0.14
2,2-$\mathrm{Cl_2C_2H}$	0.16				
2,2-$\mathrm{Cl_2C_2HCH_2}$	0.03				
Oxyalkyl					
$\mathrm{HOCH_2}$	0.05	0.10	0.01		
$\mathrm{MeOCH_2}$	0.07				
$\mathrm{MeCHOHCH_2}$	−0.01				
$\mathrm{Me_2COHCH_2}$	−0.04				
MeCHOH	0.02				
PhCHOH	0.08				
Other Substituted Alkyl					
$\mathrm{NCCH_2}$	0.18	0.23	0.24		0.21
$\mathrm{PhNHCOCH_2}$	0.00				
$\mathrm{H_2NCOCH_2}$	0.05				
$\mathrm{H_2NCH_2}$	0.08				
$\mathrm{AcNHCH_2}$	0.07				
$\mathrm{MeO_2CCH_2}$	0.17				
$\mathrm{EtO_2CCH_2}$	0.13				
$\mathrm{HSCH_2}$	0.10				
$\mathrm{PhCH_2SCH_2}$	0.06				
$\mathrm{Me_3SiCH_2}$	−0.05	−0.11	−0.07		−0.14
Carbonyl					
Ac	0.29	0.28	0.23		
$\mathrm{CO_2Me}$	0.34	0.30			
$\mathrm{CO_2Et}$	0.34	0.30	0.21		
$\mathrm{CONH_2}$	0.27			0.24	
PhNHCO	0.25				
Aza					
EtOCONH	0.32				
HCONH	0.26				
EtCONH	0.25				
BzNH	0.27		0.21	0.29	
$\mathrm{H_2NCONH}$	0.21				
PhNAc	0.22				
1-$\mathrm{C_{10}H_7NAc}$	0.26				
2-$\mathrm{C_{10}H_7NAc}$	0.27				
$\mathrm{PhSO_2NH}$	0.32				
Oxa					
EtO	0.27			0.27	
PrO	0.27	0.28			
i-PrO	0.26				
BuO	0.27	0.31			
s-BuO	0.26				
Cy-pentyloxy	0.26				
Cy-hexyloxy	0.29				
PhO	0.39	0.38	0.37	0.38	
$\mathrm{O_2NO}$	0.62				
$\mathrm{Me_2C{=}NO}$	0.29				
Thia					
SH	0.26	0.25	0.18		
MeS	0.25	0.19	0.14		
EtS	0.25				
PrS	0.24				
i-PrS	0.25	0.25			
BuS	0.23				
Cyclohexyl-S	0.31				
$\mathrm{PhCH_2S}$	0.25				
$\mathrm{Ph(CH_2)_2S}$	0.06				
$\mathrm{Ph_3CS}$	0.11				
PhS	0.30				
NCS	0.55				
$\mathrm{H_2N(CO)S}$	0.33				
Sulfonyl					
$\mathrm{MeSO_2}$	0.59	0.59		0.54	
$\mathrm{EtSO_2}$	0.60				
$\mathrm{PrSO_2}$	0.59				
i-$\mathrm{PrSO_2}$	0.59				
$\mathrm{PhSO_2}$	0.57				
Other					
$\mathrm{Me_3Si}$	−0.13	−0.12			
$\mathrm{PhMe_2Si}$	−0.14				
$\mathrm{Me_3SiOSiMe_2}$	−0.13				
$\mathrm{N_3}$	0.42				
PhSO	0.52				
Cyclohexyl-Se	.38				
SeCN	0.58				
Ionic					
$\mathrm{CO_2^-}$	−0.17		−0.35	−0.15	
$\mathrm{AsO_3H^-}$	0.01				
$\mathrm{SO_3^-}$	0.13		0.25	0.03	
$\mathrm{Me_3N^+}$	0.73	0.92	0.93		
$\mathrm{Me_2NH^+}$	0.70				
$\mathrm{MeNH_2^+}$	0.60				
$\mathrm{NH_3^+}$	0.60	0.60	0.58		
$\mathrm{CH_2CO_2^-}$	0.01				
$\mathrm{CH_2NH_3^+}$	0.36	0.25	0.25		
$\mathrm{EtNH_2^+}$	0.60				
$\mathrm{PrNH_2^+}$	0.60				
$\mathrm{BuNH_2^+}$	0.60				
i-$\mathrm{BuNH_2^+}$	0.60				

is used. The values of r and s obtained for the series at 25° which includes the pK_{a_1} of malonic acid (correlated by a statistical factor of 0.5) are 0.989 and 0.131, respectively, slightly worse than those given in Table III for the series omitting this point. The value of σ_I calculated for the CO_2H group on the basis of series 1f is 0.39. This value seems somewhat high. The use of eq. 3 gives a value of 0.33. The carbomethoxy and carbethoxy groups have σ_I values of 0.34 and 0.34, respectively (Table IV). Presumably, the value of σ_I will be about the same as the values for CO_2Me and CO_2Et.

Effect of Temperature on the Reaction Constant.—The values of ρ obtained for series 1a–k permit a test of the relationship

$$\rho = \frac{m}{T} + c \qquad (6)$$

which has been proposed by a number of authors, and most recently by Hepler.[5] Correlation of the ρ values for series 1a–k with eq. 6 gives very poor results ($r = 0.579$, $t = 2.129$, $n = 11$). The ρ values seem by inspection more likely to fit a parabolic relationship. This is in accord with the observation that ionization constants of aliphatic carboxylic acids fit the parabolic equation

$$\log K = \log K_m - p(T - T_m)^2 \qquad (7)$$

where K_m is the maximum value of K, occurring at the maximum temperature T_m.[6] Thus, for these series of ionization constants, eq. 6 is not obeyed.

(5) L. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963).

(6) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 69.

Solvolysis of Substituted γ-Butyrolactones and δ-Valerolactones

OWEN H. WHEELER AND ELSIE E. GRANELL DE RODRIGUEZ

Department of Chemistry and Puerto Rico Nuclear Center, University of Puerto Rico at Mayaguez,[1] Mayaguez, Puerto Rico

Received August 30, 1963

Methyl substitution of γ-butyrolactone results in a reduction of the equilibrium constants for hydrolysis. This is due to a combination of the enhancement of the rate of ring closure and reduction in the ease of ring opening by substitution, the first factor being the more important. The results for the δ-valerolactones confirm these findings.

A previous publication[2] reported the influence of methyl substitution on the rate of saponification of γ-butyrolactone in 92.3% ethanol–water. Shechter and co-workers[3] have carried out similar studies in 50% dimethoxyethane–water and also have measured the basic hydrolysis of several δ-valerolactones. This paper reports measurements of the equilibrium constants of substituted γ-butyro- and δ-valerolactones in acid solution. The values of the rate constants of acid-catalyzed hydrolysis of γ-butyrolactone and γ-methylbutyrolactone (where the equilibrium constants were sufficiently large) and of the δ-valerolactones were determined also (see Tables I and II).

TABLE I

HYDROLYSIS OF BUTYROLACTONES[a]

Butyrolactone	25°, l. mole^{-1} min.$^{-1}$		0°, l. mole^{-1} min.$^{-1}$	
	$K_H \times 10^2$	$k_H \times 10^2$	$K_H \times 10^2$	$k_H \times 10^2$
	34.7 (37.2)	2.20 (1.40)	21.9	0.211
α-Methyl-	2.45 (4.9)	(1.0)		
β-Methyl-	4.81			
γ-Methyl-	7.81	1.58 (1.0)	7.46	0.184
α,α-Dimethyl-	<1			
β,β-Dimethyl-	<1			
γ,γ-Dimethyl-	2.8 (1.8)	(0.8)		

[a] Present work, in 0.025 M hydrochloric acid; values in parenthesis in 1 N nitric acid from H. Sibelius, Inaugural dissertation, Lund, 1927, quoted by W. Hückel ["Theoretical Principles of Organic Chemistry," Vol. II, Elsevier, New York, N. Y., 1958, p. 895] as equilibrium constants for cyclization ($1/K_H$).

TABLE II

HYDROLYSIS OF VALEROLACTONES[a]

Valerolactone	K_H	k_H
	16.3 (10.0)	2.16 (2.38)
β-Methyl-	0.92	1.92
δ-Methyl-	2.64 (3.72)	1.16 (2.07)
β,β-Dimethyl-	0.090	0.734
δ,δ-Dimethyl-	2.31 (3.0)	0.125 (0.155)

[a] All data at 25°, l. mole^{-1} min.$^{-1}$; present work in 0.020 M hydrochloric acid; values in parenthesis in 1 N nitric acid from H. Sibelius, Inaugural dissertation, Lund, 1927, quoted by W. Hückel ["Theoretical Principles of Organic Chemistry," Vol. II, Elsevier, New York, N. Y., 1958, p. 895] as equilibrium constants for cyclization ($1/K_H$).

In general, substitution, particularly *gem*-disubstitution, increases the rate of ring formation.[4] However, cyclization reactions are usually irreversible, and lactonization is the only simple example of such reactions which are reversible. Here alkylation can effect both the forward and reverse reactions.

γ-Butyrolactones.—The equilibrium constants for hydrolysis (K_H) of the γ-butyrolactones (Table I; $K_H = [A]/[L]$ for $L + (H_2O) \rightleftharpoons A$) decrease with methyl substitution in the order $H \gg \gamma\text{-}CH_3 > \beta\text{-}CH_3 > \alpha\text{-}CH_3 \sim \gamma,\gamma\text{-}(CH_3)_2 \gg \alpha,\alpha\text{-}(CH_3)_2 \sim \beta,\beta\text{-}(CH_3)_2$, the last two lactones being essentially unhydrolyzed. *gem*-Dialkyl effect favoring the cyclized product has been explained[4] as being due to a combination of a favorable enthalpy effect, since the number of gauche interactions in the ring compound is less than in the open-chain derivative, and an entropy effect resulting from increased restriction to internal rotation in the acyclic compound on chain branching. For γ-hydroxy-

---

(1) The Puerto Rico Nuclear Center is operated for the Atomic Energy Commission by the University of Puerto Rico.

(2) O. H. Wheeler and D. S. Gamble, *J. Org. Chem.*, **26**, 3221 (1961).

(3) (a) H. Shechter, private communication; (b) C. A. Matussak, thesis, Ohio State University, 1957; (c) T. J. Dougherty, thesis, Ohio State University, 1959.

(4) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960).