In a control experiment to determine the optical stability of the *endo*-ester, pyrolysis of a sample prepared with diazomethane from acid of $[\alpha]^{25}D$ +58.9° under the usual conditions (2.2 g. in 32 ml. of decalin heated at 171° for 4 hours), followed by the customary work-up (saponification, iodolactone formation, chromatography of the iodolactone, which gave material of m.p. 75–76°, and reduction with zinc and acetic acid) gave *endo*-acid, $[\alpha]^{25}D$ +55.5°, m.p. 103–110°.

Thermal Isomerization of the *exo*-Cyclopentadiene–Methyl Methacrylate Adduct IIA-2b in Polymethyl Methacrylate.— A solution of 27.4 g. of (—)-IIA-2b (prepared from acid of $[\alpha]^{25}D$ −48.8°) in 420 ml. of freshly distilled methyl methacrylate was treated with 1.2 g. of benzoyl peroxide, sealed in two glass tubes, warmed to about 50° for 15 minutes, and allowed to stand overnight at room temperature. The tubes were cracked away from the solid polymer by tapping with a hammer, the polymer was crushed and finally milled to particles about 2 mm. in diameter. This material was distributed into fourteen Carius tubes and heated at 171° for 8.25 hours. The contents, which had partially flowed together, were removed, repulverized, and extracted with 2.5 l.

of boiling acetone in a Soxhlet extractor. About 50% of the polymer dissolved. The acetone solution was filtered to remove insoluble polymer, the filtrate was treated with 2 l. of anhydrous methanol and evaporated to a volume of 500 ml. under a 14-in. Vigreux column. Another 500 ml. of methanol were added and the precipitated polymer was filtered off. Evaporation of the filtrate to a volume of 75 ml. produced more precipitate, which was again filtered off. Further concentration of the filtrate and distillation gave material which, after having been taken up in ether, washed with bicarbonate solution and water, dried over magnesium sulfate and distilled (101–102°/39 mm.), amounted to 5.3 g. (19%) of mixed esters. By vapor chromatography, the composition was 67.9% *exo* and 32.1% *endo*. The mixed esters were saponified and the acids separated by the iodolactone procedure as previously described. The recovered *exo*-acid had $[\alpha]^{25}D$ −19.4°. The iodolactone, after chromatography, was racemic and gave upon reduction racemic *endo*-acid, m.p. 107–110°. Esterification with diazomethane gave *endo*-ester which was homogeneous by vapor chromatography.

Kinetics of Reactions in Moderately Concentrated Aqueous Acids. I. Classification of Reactions[1,2]

BY JOSEPH F. BUNNETT

Plots of (log k_ψ + H_0), or appropriate other function for more basic substrates, against log a_{H_2O} are generally linear or approximately so. The slopes define a parameter, called w, which is useful for the classification of reactions. Plots of (log k_ψ − log [HX]) *versus* log a_{H_2O} are also often linear, and their slopes define a complementary parameter. w^*. w- and w^*-values have been reckoned from literature data for a large number of reactions. Most w-values fall between −2 and +7, and they show no particular tendency to cluster about magnitudes corresponding to the "ideal" Zucker–Hammett categories. Classification according to the Zucker–Hammett categories requires arbitrary decisions in some cases and in general obscures subtle and important differences which are revealed by w- and w^*-values. The latter are therefore recommended for use in the precise classification of acid-catalyzed reactions.

The rates of acid-catalyzed reactions depend on the acid concentration. But they do not all depend in the same way. Some reactions accelerate more rapidly than others as the acid concentration is increased, some pass through a rate maximum at a particular acid concentration and some actually go steadily *slower* as the acid concentration is increased above, say, 1 *M*.

Interpretation of these phenomena is of course a challenge, and has further interest because of the reward of insight into reaction mechanisms. To date, the most widely used interpretation has been the Zucker–Hammett hypothesis.[3,4] This hypothesis stems from Hammett's important observation that, when rate coefficients for a reaction at several mineral acid concentrations above 1 *M* are available, log k_ψ[5] is sometimes linearly related to −H_0 and other times linearly related to log [HX]. Reactions in the former category give curves when log k_ψ is plotted against log [HX], and *vice versa*.

Hammett postulated that when log k_ψ was linear with −H_0, transformation of the protonated substrate (SH+) to transition state did not involve reaction with water, and that when log k_ψ was linear with log[HX] transformation of SH+ to transition state required a molecule of water.

These principles seemed to work pretty well,[6] but in time several inconsistencies were noted. Recently the Zucker–Hammett hypothesis has been sharply criticized.[7–11] Indeed, this subject has become so troubled that R. P. Bell said in the preface of a recent book,[12] "I . . . had originally intended to add a chapter on reaction kinetics in these (concentrated) solutions; however, this was finally abandoned in view of the confused state of the subject at present."

One difficulty with the Zucker–Hammett approach is that few reactions fit the two categories perfectly. A perfect fit would be a straight line

(1) Financial support by the Office of Ordnance Research, U. S. Army, and by the National Science Foundation (Grant No. G-6210) is gratefully acknowledged. Presented in part to the Eighth Conference on Reaction Mechanisms, Princeton, N. J., Sept., 1960.

(2) Described tersely in a preliminary Communication: J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960).

(3) L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 273–277.

(5) k_ψ symbolizes the pseudo-first-order rate coefficient. Since the catalyzing acid is, in the systems under consideration, always in great excess with respect to the substrate, pseudo-first-order kinetics are the rule (at any fixed acid concentration).

(6) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957). This article, written in the heyday of the Zucker–Hammett hypothesis, is the best available treatment of it in respect to both theory and application.

(7) E. Grunwald, A. Heller and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

(8) R. W. Taft, Jr., N. C. Deno and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 306 (1958).

(9) J. Koskikallio and E. Whalley, *Can. J. Chem.*, **37**, 788 (1959).

(10) H. Kwart and A. L. Goodman, *J. Am. Chem. Soc.*, **82**, 1947 (1960).

(11) L. Melander and P. C. Myhre, *Arkiv. Kemi*, **13**, 507 (1959).

(12) R. P. Bell. "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.
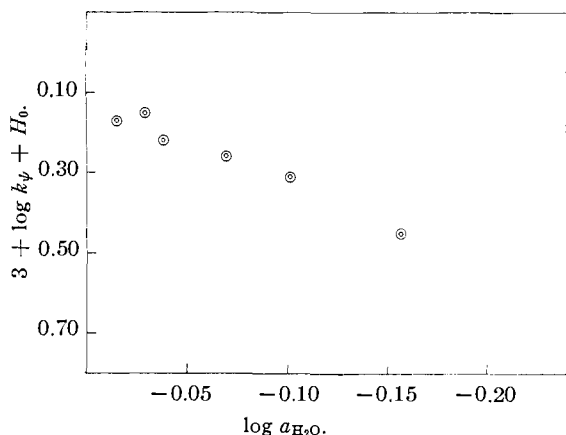
Fig. 1.—Hydrolysis of methylal in perchloric acid solutions; plot of (log k_ψ + H_0) against log a_{H_2O}. The slope, w, is −2.0; reaction 1c, Table I.
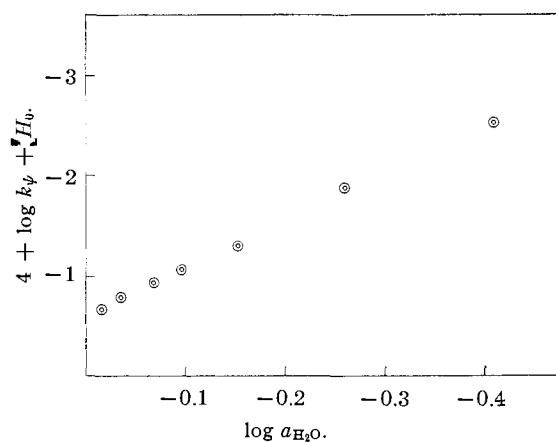

Fig. 3.—Hydrolysis of nicotinamide in hydrochloric acid solutions; plot of (log k_ψ + H_0) against log a_{H_2O}. The slope, w, is +4.8; reaction 39, Table I.
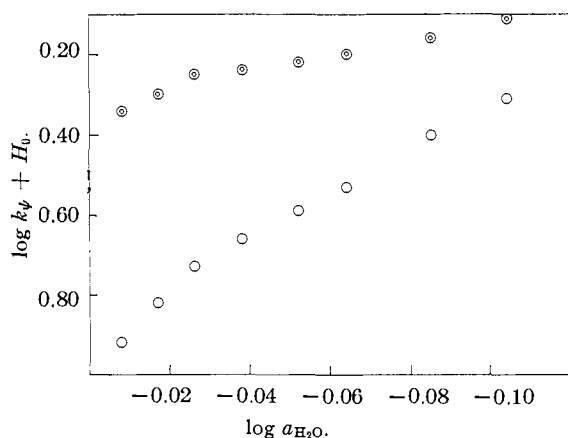

Fig. 2.—Hydrolysis of γ-butyrolactone (open circles) and lactonization of γ-hydroxybutyric acid (bulls-eyes) in hydrochloric acid solutions; plots of (log k_ψ + H_0) against log a_{H_2O}. The vertical scales are adjusted to bring the two sets of data together in the same plot. Slopes (w) are +2.2 for lactonization and +6.1 for hydrolysis; reactions 74a and 83a, Table I.

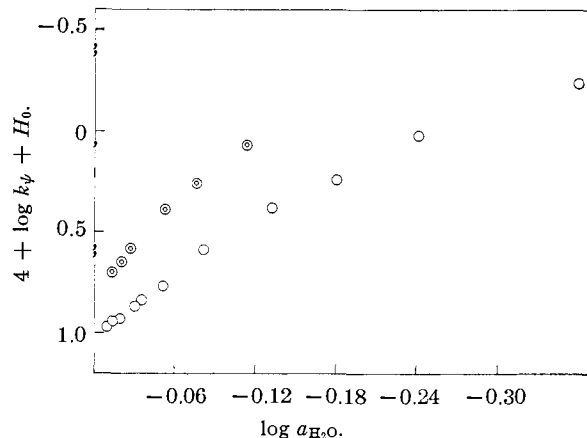Fig. 4.—Enolization of acetophenone in sulfuric acid (open circles) and perchloric acid (bulls-eyes); plots of (log k_ψ + H_ψ) against log a_{H_2O}. The slopes, w, are +3.6 and +6.4, respectively; reaction 77, Table I.

with slope 1.00 when log k_ψ was plotted against −H_0 or log [HX]. When plots were linear, slopes were often greater or less than unity, say, 1.16 or 0.90. Many so-called linear plots were not truly straight, and some reactions did not give linear plots of log k_ψ against either −H_0 or log [HX]. In the latter cases, researchers usually placed the reaction in whichever category it resembled more closely. Placing reactions in one or another of the two categories, and letting the matter stand at that, had the unfortunate effect of obscuring subtle differences of possibly great importance. The two categories became, as it were, two Procrustean beds.

Classification According to w-Values.—I now wish to present a new system of classification of acid-catalyzed reactions occurring in mineral acids of concentration 1 M and greater. This is based on my discovery that, for most such reactions, plots of (log k_ψ + H_0) versus log a_{H_2O} are linear or approximately so. Examples are shown in Figs. 1–4.[13] The slope in such a plot constitutes a

parameter, called w, which describes the manner in which the particular reaction responds to catalysis by strong mineral acids. In the cases I have examined, w-values have ranged from about −8 to +9 although most lie between −2 and +7.

Rather than being assigned to one set category or another, reactions are classified according to their w-values. The w-value is computed objectively from the experimental data with use of H_0 and log a_{H_2O} values from the literature. No subjective decision is required in arriving at this index parameter, although (as discussed below) some care must be observed in using it in the few cases in which the plots show noticeable curvature.

Plotting (log k_ψ + H_0) against log a_{H_2O} amounts to considering the extent to which a plot of log k_ψ versus −H_0 deviates from the "ideal" slope of 1.00, as a function of log a_{H_2O}. (The activity of water diminishes steadily as acid concentration increases, and log a_{H_2O} becomes steadily more

(13) In Figs. 1–4, and in all other plots of this new type which I have constructed, both the ordinate and the abscissa are inverted; more positive values are at the bottom or left, and more negative at the top or right. This places points for the more familiar region of low acid concentration at the left side of the plot. Apparent positive slopes are, of course, truly positive.

TABLE I

CORRELATION OF REACTION RATES IN MINERAL ACIDS WITH THE ACTIVITY OF WATER

Reaction	Reaction,[a] mineral acid, temp., °C.	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w*	σ_w	σ_y	r	Type of deviation from linearity[g]	Ref. pp. 4963, 4964
	A. Reactions of acetals													
1a	Methylal, HCl, 25.0	0.4– 3.9	6	A	−5.26	0.68	0.06	0.967					S	22
1b	H₂SO₄, 25.0	1.2– 2.0	3	A	−0.09	.59	.008	.150						22
1c	HClO₄, 25.0	0.9– 4.3	6	A	−2.04	.19	.02	.982						22
2a	Ethylal, HCl, 0.0	.5– 2.9	4	A	−7.86	.48	.02	.996						23
2b	HCl, 10.0	.5– 2.9	4	A	−7.18	.49	.02	.995						23
3a	Chloroacetal, HCl, 25.0	1.2– 3.7	3	A	−6.06	1.24	.06	.980					S	24
3b	HClO₄, 25.0	0.9– 3.6	4	A	−1.06	0.77	.06	.696					S	24
4	Methoxymethyl formate, HCl, 25.0	.6– 2.4	6	A	+1.24	.60	.02	.719					S	25
5a	Methoxymethyl acetate, HCl, 25.0	.6– 5.0	11	A	−2.39	.23	.03	.959					S	25
5b	H₂SO₄, 25.0	.7– 3.3	5	A	−0.67	.54	.04	.579					S	25
6	Ethoxymethyl acetate, HCl, 25.0	.6– 2.4	6	A	−3.57	.55	.02	.956					S	25
7a	Trioxane depolymerization, HCl, 25.0	.6– 5.9	22	A	−2.10	.20	.05	.919					D	26
7b	HCl, 30	5.0– 9.0	5	A	−0.76	.10	.02	.973						27
7c	HCl, 40	3.0– 7.0	5	A	−0.82	.22	.04	.908						27
7d	HCl, 50	2.0– 6.0	5	A	−1.11	.27	.04	.923						27
7e	HCl, 60	1.0– 4.0	4	A	−2.46	.42	.03	.972						27
7f	H₂SO₄, 25.0	0.5– 4.6	12	A	−1.02	.09	.02	.966						26
7g	HClO₄, 25.0	.8– 5.1	13	A	−1.96	.14	.04	.974					D	26
8a	Paraldehyde depolymerization, HCl, 25.0	.7– 3.1	9	A	−4.32	1.10	.06	.830					S	28
8b	H₂SO₄, 25.0	.5– 2.1	5	A	−5.29	1.58	.05	.888					S	28
8c	HClO₄, 25.0	.9– 2.4	8	A	−3.84	1.50	.06	.721					S	28
9	Methyl α-D-glucopyranoside, HClO₄, 72.9	.9– 3.7	5	A	+1.73	0.21	.02	.978						29a
10	Methyl β-D-glucopyranoside, HClO₄, 72.9	.9– 2.7	4	A	+1.61	0.40	.02	.945						29a
11	Phenyl α-D-glucopyranoside, HClO₄, 57.4	1.0– 2.7	3	A	+2.99	1.37	.05	.909						29a
12a	Phenyl β-D-glucopyranoside, HClO₄, 72.9	0.8– 2.9	5	A	+1.42	0.27	.01	.950						29a
12b	t-Butyl β-D-glucopyranoside, HClO₄, 24.7	0.5– 3.3	7	A	−5.01	.48	.03	.978						29b
12c	o-Hydroxymethylphenyl β-D-glucopyranoside, HClO₄, 72.6	0.9– 3.0	5	A	+1.07	.18	.01	.957						29b
12d	Methyl α-2-deoxy-D-glucopyranoside, HClO₄, 44.5	1.0– 2.1	4	A	−1.75	1.01	.02	.763						29b
12e	Methyl β-2-deoxy-D-glucopyranoside, HClO₄, 25.0	1.0– 2.0	3	A	−1.63	0.98	.02	.869						29b
12f	Methyl α-D-mannopyranoside, HClO₄, 73	1.0– 3.5	6	A	+0.41	.23	.02	.666						29c
12g	Maltose, HClO₄, 72.6	1.5– 3.0	4	A	+3.02	.52	.02	.972						29b
12h	Lactose, HClO₄, 72.6	0.9– 3.0	5	A	+2.95	.46	.02	.964						29b
13a	Sucrose, HCl, 0.0	0.6– 5.8	10	A	−0.43	.19	.04	.624						30
13b	HCl, 10.0	1.1– 4.6	5	A	−.39	.22	.02	.716						30
13c	HCl, 15.0	1.1– 2.1	3	A	−.80	.15	.003	.982						30
13d	HCl, 20.0	1.0– 3.0	5	A	−.68	.08	.003	.980						30
13e	HCl, 25.0	0.5– 2.1	5	A	−.43	.26	.007	.689						30

See also reactions 55, 71 and 72

No.	Compound, reaction, conditions	Range	n	Type										Ref.
14	β-Hydroxy-β-phenylpropiophenone, reverse aldol, H₂SO₄, 25.1	3.7- 6.6	4	A	-0.02	0.44	0.09	0.038						31
15	4-(p-Methoxyphenyl)-4-hydroxy-2-butanone, dehydration, H₂SO₄, 25.0	1.0- 3.9	5	A	-.93	.03	.003	.998						32
16a	4-(p-Methoxyphenyl)-4-hydroxy-3-methyl-2-butanone.[h] reverse aldol, H₂SO₄, 25.0	3.5- 8.1	11	A	+.91	.10	.05	.951					I	33
16b	dehydration, H₂SO₄, 25.0	3.5- 8.1	11	A	-.11	.05	.03	.609						33
17a	2,4-Dinitrobenzyl alcohol, sulfation, H₂SO₄, 0.0	11.0-17.3	8	A	-.11	.01	.04	.959						34
17b	H₂SO₄, 25.0	10.1-14.7	7	A	+.05	.02	.02	.799						34
18	2-Butanol, oxygen exchange, HClO₄, 99.8	1.1- 3.5	5	A	+.82	.43	.03	.741						35
19	(-)-2-Butanol, racemization, HClO₄, 99.8	1.1- 2.6	3	A	+1.28	.30	.01	.976						35
20	t-Butyl alcohol, oxygen exchange, H₂SO₄, 25.0	1.0- 4.0	4	A	-2.32	.86	.08	.987					S	36
21a	t-Amyl alcohol, dehydration, H₂SO₄, 25.0	1.5- 4.1	3	A	-0.37	1.04	.09	.338					S	36
21b	HNO₃, 30.0	1.0- 4.9	6	A	+0.49	0.40	.04	.520					S	36
22a	Pinacol, rearrangement, H₂SO₄, 72.6	0.7- 6.3	4	A	+4.99	.83	.24	.973					D	37
22b	H₂SO₄, 72.9	1.3- 3.0	5	A	+1.75	.50	.02	.897					S	38
22c	H₂SO₄, 100.0	0.4- 2.2	4	A	+4.26	.42	.01	.990	(+1.00)	0.48	0.01	0.900		38
23	2-Methyl-1,2-propanediol, rearrangement, HClO₄, 72.9 See also reactions 78-80, 83	0.5- 4.3	10	A	-1.23[i]	.19	.09	.222						39

C. Hydrogen isotope exchange at aromatic carbon

No.	Compound, reaction, conditions	Range	n	Type										Ref.
24	Benzene-d, H₂SO₄, 25.0	10.7-14.7	6	A	-0.58	0.03	0.03	0.996						40
25	Toluene-4-d, H₂SO₄, 25.0	7.7-12.3	5	A	-1.03	.05	.04	.997						41
26a	4-Methylphenol-2-d, HCl, 25.0	2.0- 6.5	4	A	-1.09	.10	.02	.992						42
26b	H₂SO₄, 25.0	1.1- 6.2	6	A	-0.60	.19	.05	.847					S	43
27	4-Chlorophenol-2-d, H₂SO₄, 25.0	5.4-10.0	5	A	+.60	.28	.16	.968					D	43
28	4-Nitrophenol-2-d, H₂SO₄, 25.0	10.1-18.3	9	A	+.15	.05	.13	.795					S	43
29	Anisole-2-d, H₂SO₄, 25.0	5.2- 7.9	5	A	-.40	.11	.03	.908					S	44
30	Anisole-4-d, H₂SO₄, 25.0	3.5- 7.6	5	A	-.97	.22	.07	.929					D	44
31	1,3,5-Trimethoxybenzene-2-t, HClO₄, 25.0	0.5- 3.0	7	A	-.78	.71	.04	.445					S	45

D. Hydrolyses of amides

No.	Compound, reaction, conditions	Range	n	Type										Ref.
32a	Acetamide, HCl, 50	0.6- 5.0	8	B[j]	+2.65	0.13	0.02	0.992						18
32b	HCl, 61.0	1.0- 5.0	7	B[j]	+2.29	.15	.02	.989						46
32c	HClO₄, 95	5.9- 8.5	3	C	+1.53	.15	.06	.994						47
33a	Propionamide, HCl, 40.5	1.0-10.1	5	B[j]	+2.26	.12	.05	.996						48
33b	HCl. 59.6	1.0-10.1	5	B[j]	+2.08	.08	.04	.998						48
34a	Benzamide, HCl, 25.0	1.0- 8.6	9	B[k]	+1.18	.05	.02	.993						17
34b	HCl, 59.6	1.0- 8.5	3	B[k]	+1.22	.10	.03	.996						48
34c	H₂SO₄, 25.0	1.0- 8.0	7	B[k]	+2.02	.12	.06	.996						17
34d	HClO₄, 95	5.9- 8.5	3	C	+1.75	.13	.05	.997						47
35	p-Methoxybenzamide, HClO₄, 95	5.9- 8.5	3	C	+1.69	.18	.07	.993						47
36	m-Nitrobenzamide, HClO₄, 95	5.9- 8.5	3	B[l]	+1.23	.02	.007	1.000						47
37	p-Nitrobenzamide, H₂SO₄, 25 0	3.1- 8.0	5	B[m]	+1.26	.06	.02	0.997						17
38	Picolinamide, HCl, 85	1.0- 7.8	7	A	+4.91	.08	.02	.999	-0.63	0.07	0.02	0.969		49
39	Nicotinamide, HCl, 76.0	1.0- 8.6	7	A	+4.77	.07	.02	.999	-.58	.15	.05	.861		50

TABLE I (*continued*)

Reaction	Reaction,[a] mineral acid, temp., °C	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w^*	σ_w	σ_y	r	Type of deviation from linearity[g]	Ref.
									\(-w^*\) (or w_a)[f]					
40	Isonicotinamide, HCl, 68	1.0– 7.9	7	A	+4.94	.08	.02	1.000	− .53	.11	.03	.907		49
41	Acetylglycine, HCl, 61.0	1.0– 8.2	7	B[n]	+1.41	.06	.02	0.995						51
42	Piperazine-2,5-dione, HCl, 61.0	1.0–10.2	8	A	+5.12	.28	.14	.991	+ .35	.06	.03	.914		51
43	Acethydrazide, HCl, 61.0	1.0– 7.0	6	A	+5.11	.40	.09	.988	− .55	.52	.12	.465	S	46

E. Hydrolyses of non-carboxylic esters

Reaction	Reaction,[a] mineral acid, temp., °C	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w^*	σ_w	σ_y	r	Type of deviation from linearity[g]	Ref.
44a	2,4-Dinitrobenzyl hydrogen sulfate, H_2SO_4, 0.0	11.0–17.3	8	A	+0.61	0.03	0.08	0.992					D	34
44b	H_2SO_4, 25.0	10.1–14.7	7	A	+ .81	.04	.05	.995						34
45	d-sec-Butyl hydrogen sulfate, racemization, H_2SO_4, 25.0	6.2–10.3	4	A	− .02	.05	.03	.322						52
46	Dimethyl sulfite, $HClO_4$, 0.0	2.1– 7.2	6	A	+2.36	.14	.06	.993	−2.46	0.30	0.13	0.971	S	53
47a	Diethyl sulfite, $HClO_4$, 0.0	0.5– 7.2	12	A	+2.15	.16	.09	.974	−2.91	.10	.06	.994	D-w	53
47b	$HClO_4$, 24.9	1.0– 4.1	4	A	+3.58	.21	.02	.995	−3.82	.21	.02	.997		53
48	Ethylene sulfite, $HClO_4$, 44.6	1.1– 5.5	6	A	+4.21	.29	.06	.990	−1.94	.15	.03	.988		54
49	(−)-2,3-Butylene sulfite, $HClO_4$, 35.0	1.0– 6.0	5	A	+3.47	.23	.06	.993	−2.28	.28	.07	.978		55
50	meso-2,3-Butylene sulfite, $HClO_4$, 35.0	1.0– 6.0	6	A	+4.19	.36	.10	.985	−1.52	.10	.03	.992	D-w	55
51	Tetramethylethylene sulfite, $HClO_4$, 35.0	1.0– 5.0	5	A	+4.35	.47	.08	.983	−1.98	.03	.005	.999	D-w	55
52	Trimethylene sulfite, $HClO_4$, 35.0	0.5– 4.1	6	A	+3.93	.27	.03	.993	−3.50	.14	.02	.997		54
53	Methyl dihydrogen phosphate, $HClO_4$, 100	1.0– 9.0	9	A	+4.00[o]	.31	.29	.980	−0.08[o]	.05	.04	.522	D-w	56
54	Dimethyl hydrogen phosphate, $HClO_4$, 100	1.0– 5.0	5	A	+4.64[p]	.33	.05	.993	−1.90[p]	.25	.04	.976		57
55a	α-D-Glucose-1-(dihydrogen phosphate), H_2SO_4, 25.0	0.9– 2.4	3	A	+3.34	1.51	.05	.911					S	58
55b	$HClO_4$, 25.0	1.0– 3.4	8	A	+1.75	0.37	.03	.888					S	58

F. Reactions of ethers

Reaction	Reaction,[a] mineral acid, temp., °C	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w^*	σ_w	σ_y	r	Type of deviation from linearity[g]	Ref.
56	Diethyl ether, $HClO_4$, 120.1, 50 atm. pressure	1.1– 5.6	5	A[q]	+2.72[q]	0.18	0.04	0.993	−3.15[q]	0.28	0.06	0.988		9
57	4-(p-Sulfophenylazo)-anisole, HCl, 97.0	1.0– 9.3	9	B[r]	+2.85	.14	.06	.991	−2.19	.29	.12	.944		19
58a	4-(p-Sulfophenylazo)-1-naphthyl methyl ether, HCl, 46.0	1.0– 8.1	9	B[s]	+4.51	.12	.04	.998	−0.94	.16	.05	.911		19
58b	$HClO_4$, 46.0	1.1– 4.1	6	B[s]	+8.24	.60	.06	.989	+0.93	.46	.05	.713	D-w	19
59	1,2-Dimethoxy-2-methylpropane, rearrangement, $HClO_4$, 72.9	1.1– 4.3	4	A	−3.58	.34	.04	.991					D	39

G. Reactions of carboxylic esters

Reaction	Reaction,[a] mineral acid, temp., °C	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w^*	σ_w	σ_y	r	Type of deviation from linearity[g]	Ref.
60	Methyl formate, HCl, 25.0	2.7– 6.4	5	A	+4.21	0.28	0.04	0.993	−1.50	0.06	0.008	0.998		59
61	Methyl acetate, HCl, 25	0.5– 3.6	8	A	+5.83	.24	.02	.995	−1.47	.14	.01	.975		60
62a	Ethyl acetate, HCl, 25.0	0.7–10.2	14	A	+4.15	.09	.07	.997	−0.60	.07	.05	.923	D-w*	59
62b	H_2SO_4, 25.0	1.4– 6.8	9	A	+4.50	.21	.07	.992	(+1.12)	.10	.02	.975		59
63	Isopropyl acetate, HCl, 25.0	0.6– 8.9	6	A	+4.62	.08	.03	.999	−0.71	.13	.05	.937	D-w*	61
64	tert-Butyl acetate, HCl, 25.0	0.6– 6.9	6	A	−1.17	.31	.07	.886					D	61
65a	$C_2H_5OOCCH_2SO_3K$, HCl, 25.0	1.9–10.4	10	A	+4.52	.15	.06	.999	−0.63	.09	.05	.930		62
65b	H_2SO_4, 25.0	1.5– 5.7	4	A	+4.88	.65	.13	.982	(+1.41)	.20	.04	.981		62
66	Methyl benzoate, $HClO_4$, 90	1.0– 3.8	3	A	+7.02	.70	.06	.995	−0.13	.11	.009	.747		63
67a	Methyl mesitoate, H_2SO_4, 90	3.1– 6.1	4	A	−1.10	.84	.15	.678						63
67b	$HClO_4$, 90	1.0– 5.8	9	A	−2.47	.33	.09	.943						63
68	α-Glyceryl monobenzoate, $HClO_4$, 90	0.5– 5.8	7	A	+6.09	.27	.08	.995	− .06	.04	.01	.506	D-w	63
69	α-Glyceryl monoanisoate, $HClO_4$, 90	0.5– 5.7	6	A	+5.72	.50	.11	.989						63

70	α-Glyceryl mono-3,4,5-trimethoxybenzoate, H_2SO_4, 50	1.1– 9.7	8	B[t]	+2.91	.22	.22	.983	− .83[u]	.07	.05	.989	D-w	63
71	Methylene diacetate, HCl, 25.0	0.8– 8.0	11	A	+4.17	.06	.02	.999	−1.41	.08	.03	.987		64
72a	Ethylidene diacetate, HCl, 25.0	0.8– 8.0	11	A	+4.11	.06	.02	.999	−1.46	.07	.03	.990		64
72b	HCl, 25.0	0.7– 8.9	12	A	+3.95	.12	.07	.995	−1.22	.09	.05	.975		65
73a	β-Propiolactone, H_2SO_4, 25.0	2.0– 5.1	5	A	+0.39	.71	.10	.303						66
73b	$HClO_4$, 25.0	1.8– 5.4	8	A	−1.18	.59	.11	.634						66
74a	γ-Butyrolactone, HCl, 0	0.5– 3.9	8	A	+6.11	.60	.05	.971	−0.91	.08	.007	.976		67
74b	$HClO_4$, 5	0.8– 3.3	5	A	+8.50	.36	.02	.997	+0.38[v]	.47	.03	.429		67
75a	β-Isovalerolactone, hydrolysis, $HClO_4$, 25.0	0.8– 3.6	14	A	+0.06	.17	.02	.106						68
75b	decarboxylation, $HClO_4$, 25.0	1.6– 3.6	14	A	+6.53[w]	.38	.05	.981	−1.17[w]	.34	.04	.700		68
	See also reactions 4–6													

H. Reactions of ketones

76a	Acetone, bromination (enolization), HCl, 25.0	1.0– 8.0	8	A	+3.83	0.09	0.03	0.998	−1.66	0.08	0.02	0.994		69
76b	Acetone, iodination (enolization), HCl, 25	0.5– 2.7	5	A	+6.66	.52	.02	.991	−1.42	.08	.003	.996		70
77a	Acetophenone, iodination (enolization), H_2SO_4, 25.0	0.6– 6.4	11	A	+3.63	.19	.07	.988	$(0.00)^x$					3
77b	$HClO_4$, 25.0	0.8– 3.6	6	A	+6.35	.32	.03	.995	−1.62	.08	.007	.995		3
78	β-Hydroxy-β-phenylpropiophenone, dehydration (enolization), H_2SO_4, 25.1	2.3– 6.6	5	A	+2.76	.24	.06	.989	(−0.32)	.11	.03	.859		31
79a	4-Hydroxy-4-phenyl-2-butanone, dehydration (enolization), H_2SO_4, 25.0	0.5– 7.7	6	A	+3.17	.29	.12	.988	(+0.45)	.18	.03	.874		32
79b	$HClO_4$, 25.0	3.0– 9.3	3	A	+2.16	.71	.50	.949	−1.39	.11	.08	.997		32
80	4-Hydroxy-4-(p-nitrophenyl)-2-butanone, dehydration (enolization), H_2SO_4, 25.0	1.0– 7.3	5	A	+3.36	.25	.10	.992	(+0.39)	.13	.03	.900		32
81a	cis-Benzalacetophenone, isomerization to trans, H_2SO_4, 26.0	0.5– 5.3	5	A	+2.77	.20	.04	.992	(−0.86)	.26	.05	.883		31
81b	H_2SO_4, 38.0	.5– 5.3	3	A	+3.26	.09	.02	1.000	(−0.29)	.16	.03	.877		31
81c	$HClO_4$, 26.0	.6– 5.4	7	A	+3.19	.37	.08	0.969	−3.22	.17	.04	.993		31
	See also reactions 14–16													

I. Reactions of acid derivatives, except amides and esters

82	Benzoic acid, oxygen exchange, H_2SO_4, 73.0	1.1– 3.0	4	A	+8.81	1.38	0.07	0.977	(+3.53)	1.46	0.07	0.863	S	71
83a	γ-Hydroxybutyric acid, lactonization, HCl, 0	0.5– 3.9	8	A	+2.23	.18	.02	.981	−4.76	.22	.02	.994		67
83b	$HClO_4$, 5	.8– 3.3	5	A	+2.21	.60	.04	.905	−5.91	.94	.06	.964		67
84	N,N'-Diphenylformamidine, HCl, 25.0	.8– 5.7	10	C	+7.75	.25	.05	.996					D	72
85a	Thioacetamide, HCl, 35.0	.5– 6.2	11	B[y]	+4.15	.28	.06	.980	−1.96	.58	.12	.749	Z	18
85b	$HClO_4$, 35.0	.6– 5.0	9	B[y]	+5.43	.16	.03	.997	−1.21	.26	.05	.869	D	18
86a	Methyl benzimidate, HCl, 25.0	1.0– 6.2	6[aa]	C	+6.30	.27	.05	.996						73
86b	H_2SO_4, 25.0	1.0– 5.0	5[aa]	C	+6.57	.16	.03	.999						73
87a	Cyanamide, HNO_3, 25.0	0.6– 3.9	8	A	+1.48	.17	.01	.963					D	74
87b	HNO_3, 30.0	1.0– 3.9	7	A	+1.38	.18	.01	.961					D	74
87c	HNO_3, 25.0	0.5 –5.0	10	A	+0.80	.13	.01	.903					D	75

J. Miscellaneous reactions

88	Methyl bromide, $HClO_4$,[bb] 50	0.0– 6.0	5	C	+3.20	0.27	0.08	0.990						76
89a	Methylmercuric iodide, cleavage, H_2SO_4, 100	1.0– 5.4	6	A	+6.59	.62	.13	.983	(+2.89)	0.33	0.07	0.975	D	77
89b	$HClO_4$, 100	1.1– 7.7	7	A	+3.38	.52	.29	.946	−1.33	.23	.13	.931	D	77
90	3,3-Dimethyl-5-ketohexanoic acid, cyclization to dimedone, H_2SO_4, 130.7	7.0–10.7	6	A	+1.52	.07	.04	.995						78

TABLE I (continued)

Reaction	Reaction,[a] mineral acid, temp., °C	Acid concn. range, M	No. points	Function plotted[b]	w	σ_w[c]	σ_y[d]	r[e]	w* (or w_a)	σ_w* (or w_a)	σ_y	r	Type of deviation from linearity[g]	Ref.
91	3,3-Dimethyl-5-ketoheptanoic acid, cyclization to 3,3,6-tri-methylcyclohexan-2,5-dione, H₂SO₄, 87.8	6.1– 9.4	3	A	+1.79	.21	.08	.993						79
92	3,3-Dimethyl-5-ketoöctanoic acid, cyclization to 3,3-di-methyl-6-ethylcyclohexan-2,5-dione, H₂SO₄, 85.8	5.8–14.0	6	A	+1.18	.05	.07	.997						79
93	3,3-Dimethyl-5-ketononanoic acid, cyclization to 3,3-di-methyl-6-propylcyclohexan-2,5-dione, H₂SO₄, 86.4	7.3–12.0	3	A	+1.25	.12	.08	.996						79
94a	Benzeneboronic acid, reaction with H₂O₂, H₂SO₄, 25.1	1.1– 9.0	5	A	+1.91	.13	.08	.993					D	80
94b	HClO₄, 25.1	0.8– 8.2	6	A	+2.73	.20	.12	.989					D	80
95	Benzhydryl azide, rearr., H₂SO₄, 25.0	3.9– 7.2	8	A	+0.31	.40	.12	.301						81
96	N-Isopropylnitramine, HCl, 45	0.8– 4.4	4	A	+2.24	.04	.004	1.000						82a
97	O,N-Dimethylnitramine, HCl, 25	1.0– 5.0	5	A	-0.48	.19	.02	0.823						82a
98	Phosphoric acid, oxygen exchange, HClO₄, 100.1	1.0– 8.9	10	A	+3.36	.15	.15	.992	-0.73	.16	.15	.852	D	82b
99	NH₃D⁺, protodedeuteration, H₂SO₄, 25	6.9–11.3	3	C	+3.09	.20	.12	.998	+0.69	.06	.04	.996	D-w	82c
100	CH₃NH₂D⁺, protodedeuteration, H₂SO₄, 25	4.4– 8.9	4	C	+4.70	.27	.12	.997	+1.12	.06	.03	.997	D-w;S-w*	82c
101	(CH₃)₂ND⁺, protodedeuteration, H₂SO₄, 25	3.0– 7.9	5	C	+6.83	.53	.22	.991	+2.80	.38	.16	.973	D	82c

[a] The reaction is hydrolysis unless otherwise described. [b] The function plotted is: A, (log k_ψ + H_0), (log k_ψ - log[HX]) or (log k_ψ - log k_A) as appropriate (see text); B, [log k_ψ - log[$h_0/(h_0 + K_{SH^+})$]] or [log k_ψ - log [[HX]/$(h_0 + K_{SH^+})$]]; C, log k_ψ or (log k_ψ - log [HX] - H_0). [c] σ_w is the standard deviation of the slope. [d] σ_y is the standard deviation, in the vertical direction, from the least squares line. [e] r is the correlation coefficient. [f] w_a-values are in parentheses. [g] The type of deviation from linearity is: S, scatter; D, steadily decreasing absolute slope; I, steadily increasing absolute slope; w, w^* or w_a refers to the plot in which the deviation occurs. [h] The acetate ester was introduced, but hydrolyzed to the alcohol before the other reactions commenced. [i] If one widely variant point is omitted, w is -2.95, σ_w is 0.28, σ_y is 0.02 and r is 0.970. [j] Using K_{SH^+} = 3.0. [k] Using K_{SH^+} = 5.8. [l] Using K_{SH^+} = 30. [m] Using K_{SH^+} = 26. [n] Using K_{SH^+} = 7.0. [o] Based on the corrected (for neutral hydrolysis) values of ref. 56; when the correction was made by subtracting 1.4 × 10⁻⁶ sec.⁻¹ from each experimental rate coefficient, the resulting w-values, etc., were little changed. [p] Each rate coefficient was corrected by subtraction of the "neutral" hydrolysis coefficient, 4.13 × 10⁻⁶ sec.⁻¹. [q] When function B was plotted, making use of the K_{SH^+} value of E. M. Arnett and C. Y. Wu, J. Am. Chem. Soc., 82, 4999 (1960), there was a slight change in the last point only, not enough to affect the slope materially. [r] Using K_{SH^+} = 40. [s] Using K_{SH^+} = 5.5. [t] Using K_{SH^+} = 5000. [u] Based only on 5 points, 4.0-9.7 M. [v] But for one widely errant point, w^* would be about -0.4. [w] Each rate coefficient was corrected by subtraction of the "neutral" decarboxylation coefficient, 2.32 × 10⁻³ sec.⁻¹. [x] w_a is 0.00 for acetophenone enolization, by definition. [y] Using K_{SH^+} = 58. [z] Irregular, dog-leg plot. [aa] Data were presented graphically, and values at high acid concentrations could not be read with confidence. [bb] The medium contained 5% of acetone; since the reaction is not acid catalyzed, a datum for 0.0 M HClO₄ is included.

negative.) It is an empirical fact that the deviation is linear or approximately linear with log a_{H_2O}. If the actual plot of log k_ψ versus $-H_0$ lies above the "ideal" plot of slope unity, w is negative; this is the situation formerly described as a plot of slope greater than unity. If the actual plot falls below the "ideal," w is positive; this situation has been described as a slope less than unity.

Plots of the new type are more irregular than the better plots of log k_ψ against $-H_0$ or log [HX]. They show more scatter of individual points and occasionally a definite trend toward curvature. This is understandable inasmuch as a *difference* between two large quantities (log k_ψ and $-H_0$) is being plotted. Such a plot is naturally more sensitive to random experimental error, as well as to subtle trends in the data.

Substrates of Considerable Basicity.—For weakly basic substrates (S), the fraction converted to the protonated form (SH⁺) is proportional to h_0. This follows from the equation K_{SH^+} = [S]h_0/[SH⁺], which applies if protonation of the substrate is properly represented by the Hammett h_0 function. Plotting (log k_ψ + H_0) is, then, equivalent to plotting [log k_ψ - log (fraction substrate protonated)] against log a_{H_2O}; the two plots would have identical slopes but intercepts differing by log K_{SH^+}. For moderately basic substrates, such that a considerable fraction is protonated within the range of mineral acid concentrations used, the fraction protonated is given by $h_0/(h_0 + K_{SH^+})$.[6,14] The equivalent procedure is then to plot {log k_ψ - log[$h_0/(h_0 + K_{SH^+})$]} against log a_{H_2O}.[15]

It is with substrates of intermediate basicity that the interesting phenomenon of a rate maximum in a plot of k_ψ against [HX] is encountered. Such rate maxima have been known for some time in the case of carboxylic amide hydrolyses, and they are recognized to occur at approximately the acid concentration at which protonation of the amide is com-

(14) Basically, this type of correction is due to W. M. Schubert and H. K. Latourette, J. Am. Chem. Soc., 74, 1829 (1952).

(15) Some awkwardness may arise if K_{SH^+}, the acid dissociation constant of the protonated substrate, is not known.

plete.[16-18] Success has been claimed in treating the phenomenon with reference to the Zucker–Hammett hypothesis,[17,18] and indeed for thioacetamide hydrolysis[18] the agreement is good, but for hydrolyses of acetamide[18] and benzamide[17] it is quantitatively unsatisfactory. Figure 5 is an example of a plot of the new type for a reaction (acetamide hydrolysis) which passes through a rate maximum. Rate maxima also appear in hydrolyses of certain azo ethers, and good linear plots of the new type have been obtained.[19]

For strongly basic substrates, which are totally protonated throughout the range of mineral acid concentrations used, one simply plots $\log k_\psi$ against $\log a_{H_2O}$.[20] Fundamentally, it is $\{\log k_\psi - \log[h_0/(h_0 + K_{SH^+})]\}$ which is plotted against $\log a_{H_2O}$ with substrates of all types. The expressions used with weakly or strongly basic substrates are the special cases for K_{SH^+} much greater or much less than h_0, respectively.

Application to Data from the Literature.—The new plotting and classification procedure has been applied to several score sets of data concerning diverse reactions in moderately concentrated mineral acids. In general, good linear plots were obtained and w-values could be defined with certainty. This scrutiny of literature data is summarized in Table I, which comprises 158 sets of data concerning 108 reactions. The objective principles used in selecting data for scrutiny are stated in the Appendix. A few reactions which did not give acceptable linear plots are noted in the Appendix.

In Table I, the quality of fit to a straight line can be judged with reference to the statistical parameters σ_w, σ_y and r.[21] Unfortunately no single parameter of these three is a completely adequate criterion of quality of fit: r, the correlation coefficient, approaches unity when the fit is good except that r has low values when the absolute slope is small, even for a good approximation to a straight line. A low value for r must therefore be discounted if the slope, w, is small. σ_y, the standard deviation of individual points from the best line, is informative but must be interpreted with respect to the acid concentration range under investigation. When a relatively dilute range is covered, say 0.5–3.0 M, changes in both the y and x variables are small and σ_y tends to be small even for a mediocre fit. But when high acid concentrations are involved, say 10.0–15.0 M sulfuric acid, changes in both variables are large and σ_y may be large even for an excellent fit. σ_w, the standard deviation of the slope, is helpful but tends to be large (suggesting poor fit) if the number of points represented is small (say, 3 or 4) or if the absolute magnitude of the slope is large for a relatively small range of acid concentrations. The latter situation prevails when w has a large negative value, as in some acetal hydrolyses; a large σ_w value may be associated with an excellent r coefficient. On the other hand, σ_w is most valuable for judging the reliability of the w-value obtained.

Fig. 5.—Hydrolysis of acetamide in hydrochloric acid solutions: plot of $\{\log k_\psi - \log[h_0/(h_0 + K_{SH^+})]\}$ against $\log a_{H_2O}$. The slope, w, is $+2.3$; reaction 32b, Table I.

(23) P. M. Leininger and M. Kilpatrick, *ibid.*, **61**, 2510 (1939).

(24) M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, **77**, 3146 (1955).

(25) P. Salomaa, *Acta Chem. Scand.*, **11**, 132 (1957).

(26) R. P. Bell, K. N. Bascombe and J. C. McCoubrey, *J. Chem. Soc.*, 1286 (1956).

(27) L. K. Brice and L. P. Lindsay, *J. Am. Chem. Soc.*, **82**, 3538 (1960).

(28) R. P. Bell and A. H. Brown, *J. Chem. Soc.*, 774 (1954).

(29) (a) C. A. Bunton, T. A. Lewis, D. R. Llewellyn and C. A. Vernon, *ibid.*, 4419 (1955); (b) C. Armour, C. A. Bunton, S. Patai, L. H. Selman and C. A. Vernon, *ibid.*, 412 (1961); (c) A. J. Lawrence and C. A. Vernon, personal communication.

(30) P. M. Leininger and M. Kilpatrick, *J. Am. Chem. Soc.*, **60**, 2891 (1938).

(31) D. S. Noyce, W. A. Pryor and P. A. King, *ibid.*, **81**, 5423 (1959).

(32) D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5539 (1958).

(33) D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4324 (1958).

(34) G. Williams and D. J. Clark, *J. Chem. Soc.*, 1304 (1956).

(35) C. A. Bunton and D. R. Llewellyn, *ibid.*, 3402 (1957).

(36) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *J. Am. Chem. Soc.*, **82**, 4729 (1960).

(37) J. F. Duncan and K. R. Lynn, *J. Chem. Soc.*, 3519 (1956).

(38) C. A. Bunton, T. Hardwick, D. R. Llewellyn and Y. Pocker, *ibid.*, 403 (1958).

(39) J. B. Ley and C. A. Vernon, *ibid.*, 2987 (1957).

(40) V. Gold and D. P. N. Satchell, *ibid.*, 3619 (1955).

(41) V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1956).

(42) V. Gold and D. P. N. Satchell, *ibid.*, 3622 (1955).

(43) V. Gold and D. P. N. Satchell, *ibid.*, 3609 (1955).

(44) D. P. N. Satchell, *ibid.*, 3911 (1956).

(45) A. J. Kresge, personal communication.

(46) J. T. Edward, H. P. Hutchison and S. C. R. Meacock, *J. Chem. Soc.*, 2520 (1955).

(47) J. A. Leisten, *ibid.*, 765 (1959).

(48) B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **20B**, 73 (1942).

(49) H. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **57**, 900 (1953).

(50) H. H. G. Jellinek and A. Gordon, *J. Phys. Colloid Chem.*, **53**, 996 (1949).

(51) J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2007 (1957).

(52) N. C. Deno and M. S. Newman, *J. Am. Chem. Soc.*, **73**, 1920 (1951).

(53) C. A. Bunton, P. B. D. de la Mare and J. G. Tillett, *J. Chem. Soc.*, 1766 (1959).

(54) C. A. Bunton, P. B. D. de la Mare and J. G. Tillett, *ibid.*, 4754 (1958).

(55) C. A. Bunton, P. B. D. de la Mare, A. Lennard, D. R. Llewellyn, R. B. Pearson, J. G. Pritchard and J. G. Tillett, *ibid.*, 4761 (1958).

(56) C. A. Bunton, D. R. Llewellyn, K. G. Oldham and C. A. Vernon, *ibid.*, 3574 (1958).

(57) C. A. Bunton, M. M. Mhala, K. G. Oldham and C. A. Vernon, *ibid.*, 3293 (1960).

(58) C. A. Bunton, D. R. Llewellyn, K. G. Oldham and C. A. Vernon, *ibid.*, 3588 (1958).

(59) R. P. Bell, A. L. Dowding and J. A. Noble, *ibid.*, 3106 (1955).

(16) Reference 4, p. 365.

(17) J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957).

(18) D. Rosenthal and I. T. Taylor, *J. Am. Chem. Soc.*, **79**, 2684 (1957).

(19) J. F. Bunnett and E. Buncel, *ibid.*, **82**, 1117 (1960).

(20) The simple plot of $\log k_\psi$ versus $\log a_{H_2O}$ is also used with substrates of vanishing basicity if the reaction is not catalyzed by acids. An example is hydrolysis of methyl bromide (reaction 88, Table I).

(21) G. W. Snedecor, "Statistical Methods," 3rd ed., Iowa State College Press, Ames, Iowa, 1940; W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

(22) D. McIntyre and F. A. Long, *J. Am. Chem. Soc.*, **76**, 3240 (1954)
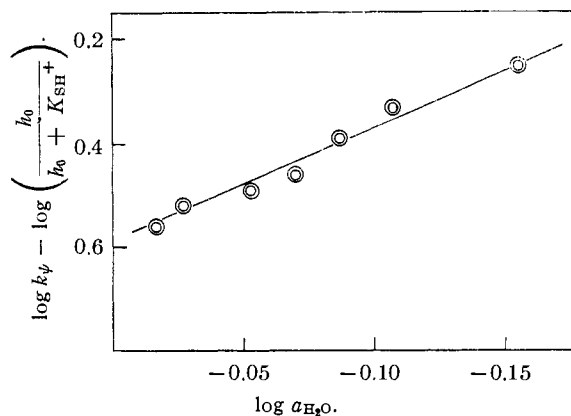
A tendency for like reactions to have like w-values may be noted in Table I. Thus, w is typically negative for acetal hydrolyses, about $+1$ to $+2.5$ for carboxylic amide hydrolyses, and about $+4$ to $+6$ for carboxylic ester hydrolyses. Divergences from typical values can sometimes be associated with known differences in mechanism, as in the cases of t-butyl acetate (reaction 64) and methyl mesitoate (reaction 67). One is caused to wonder whether other divergences may also be indicative of changes in mechanism; for example, glucoside hydrolyses (reactions 9–12) have w-values atypical for acetal hydrolysis, and w for hydrolyses of several amides (reactions 38–40,43) are unusually high.

Some dependence of w on the mineral acid can be seen. When w is positive, it is often higher in perchloric acid than in sulfuric, and higher in sulfuric than in hydrochloric. Most of the variation is within one or two w-units. However, acetal hydrolyses in hydrochloric acid solutions have w-values of much greater (negative) magnitude than in other acids.

No great dependence of w on temperature is evident. All the computations underlying Table I are based on H_0 and a_{H_2O} values for 25°, yet many of the reactions were performed at higher or lower temperatures. The ideal of computing w for each reaction from H_0 and a_{H_2O} data for the same temperature is not accessible at present because the necessary data are not available. In cases where the same reaction or closely related reactions have been studied at more than one temperature (e.g., reactions 2, 13, 32–34, 90–93), variation of w with temperature is random and generally within the standard deviation of the w-values. One does not know to what extent this represents fortuitous matching of changes in H_0, a_{H_2O} and the reaction itself.

(60) M. Duboux and A. de Sousa, *Helv. Chim. Acta*, **23**, 1381 (1940).

(61) P. Salomaa, *Suomen Kemi*, **B32**, 145 (1959).

(62) R. P. Bell and D. J. Rawlinson, *J. Chem. Soc.*, 4387 (1958).

(63) C. T. Chmiel and F. A. Long, *J. Am. Chem. Soc.*, **78**, 3326 (1956).

(64) P. Salomaa, *Acta Chem. Scand.*, **11**, 247 (1957).

(65) R. P. Bell and B. Lukianenko, *J. Chem. Soc.*, 1686 (1957).

(66) F. A. Long and M. Purchase, *J. Am. Chem. Soc.*, **72**, 3267 (1950).

(67) F. A. Long, F. B. Dunkle and W. F. McDevit, *J. Phys. Colloid Chem.*, **55**, 829 (1951).

(68) H. T. Liang and P. D. Bartlett, *J. Am. Chem. Soc.*, **80**, 3585 (1958).

(69) G. Archer and R. P. Bell, *J. Chem. Soc.*, 3228 (1959).

(70) D. P. N. Satchell, *ibid.*, 2878 (1957).

(71) C. A. Bunton, D. H. James and J. B. Senior, *ibid.*, 3364 (1960).

(72) R. H. DeWolfe, *J. Am. Chem. Soc.*, **82**, 1585 (1960).

(73) J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2009 (1957).

(74) M. J. Sullivan and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **67**, 1815 (1945).

(75) G. Grube and G. Schmid, *Z. physik. Chem.*, **119**, 19 (1926).

(76) C. G. Swain and R. E. T. Spalding, *J. Am. Chem. Soc.*, **82**, 6104 (1960).

(77) M. M. Kreevoy, *ibid.*, **79**, 5927 (1957).

(78) T. Henshall, W. E. Silbermann and J. G. Webster, *ibid.*, **77**, 6656 (1955).

(79) W. E. Silbermann and T. Henshall, *ibid.*, **79**, 4107 (1957).

(80) H. G. Kuivila, *ibid.*, **77**, 4014 (1955).

(81) C. H. Gudmundsen and W. E. McEwen, *ibid.*, **79**, 329 (1957).

(82) (a) P. Bruck and A. H. Lamberton, *J. Chem. Soc.*, 4198 (1957); (b) C. A. Bunton, D. R. Llewellyn, C. A. Vernon and V. A. Welch, *ibid.*, 1636 (1961); (c) M. T. Emerson, E. Grunwald, M. L. Kaplan and R. A. Kromhout, *J. Am. Chem. Soc.*, **82**, 6307 (1960).

Relationship of w-Values to the Zucker–Hammett Categories.—Reactions giving "linear" plots of log k_ψ against $-H_0$ have w-values ranging from about $+2$ to large negative values. If the aforesaid plots have slope unity, w is zero. If the slope exceeds unity, w is negative. If it is less than unity, w is positive. To illustrate, methylal hydrolyses in hydrochloric acid and in perchloric acid have w of -5.3 and -2.0 compared to Zucker–Hammett slopes of 1.25 and 1.08, respectively. Lactonization of γ-hydroxybutyric acid in hydrochloric or perchloric acid[67] has w of $+2.2$, and a Zucker–Hammett slope of 0.90.

Reactions giving linear plots of log k_ψ against log[HX] with unit slope usually have w-values of $+5$ or higher. To wit, for γ-butyrolactone hydrolysis[67] in perchloric acid (74b),[83] the Zucker–Hammett slope is 1.00 and w is $+8.5$. Reactions of w about $+3$ to $+4$ fall in between the Zucker–Hammett categories. The in-between character of hydrolyses of methyl formate (60) and ethyl acetate[59] (62) and of alkyl sulfites[53] (46–52) have received specific comment.

A scan of Table I reveals that there is no particular tendency for w-values to group within the two ranges corresponding to the Zucker–Hammett classifications. They are fairly evenly distributed from -2 to $+8$. Rather than two well defined classes, there are many gradations. In these circumstances it is better to eschew the Zucker–Hammett categories for purposes of serious classification and to let the response of each reaction to catalysis by concentrated acids be represented by its w-values.

Deviations from Linearity.—Plots of the new type occasionally show random scatter or persistent curvature. The former, when notable, is designated by "S" in the second column from the right in Table I. Curvature, when encountered, is nearly always in the direction of decreasing absolute slope with increasing acid concentration; such is designated by "D" in the same column. The incidence of curvature is greatest when w has a high positive value ($> +4.5$). The plots in Fig. 4 show curvature.

When there is curvature, w-values are unfortunately dependent on the range of acid concentrations employed. When the range is short and in the dilute region, w tends to be high; when it is long or in a more concentrated region, w tends to be low. w-Values from such reactions must therefore be interpreted with caution, especially if fine distinctions (based on differences of perhaps one w-unit) are taken as evidence of reaction mechanism. It should be noted that latent curvature may not make itself evident if the range of acid concentrations represented is short.

Mixed Reactions.—The w-value reckoned from rate coefficients which represent the sum of two competing reactions of the same substrate is intermediate between the w's of the component reactions. β-Isovalerolactone (75) undergoes, in perchloric acid, both hydrolysis to the hydroxy acid and decarboxylation to isobutylene. Liang and Bartlett[68] were able to dissect the total rate

(83) Numbers in parentheses following the name of a reaction refer to its location in Table I.

coefficients into components representing the contributing reactions. In 0.8 M perchloric acid, hydrolysis (w = $+0.1$) is about three times as fast as decarboxylation (w = $+6.5$). As acid concentration is increased, the reaction of lower w accelerates more quickly and by 3.6 M is some 14 times faster. The w-value ($+0.6$) for the sum of the two reactions is close to that of the dominant reaction.

Salomaa[25,84] has presented evidence that the hydrolysis of methoxymethyl formate (4) is partly unimolecular, as in hydrolysis of acetals and alkoxymethyl acetates, and partly "bimolecular," as in hydrolysis of most esters. The two mechanisms presumably involve scission of alkyl–oxygen and acyl–oxygen bonds, respectively. The w-values to be expected of the two are suggested by w of -2.4 for methoxymethyl acetate hydrolysis (5a) and $+4.2$ for methyl formate hydrolysis (60), both in hydrochloric acid. The experimental w for methoxymethyl formate hydrolysis, $+1.2$, is about half way between. To the alert eye, such a discrepancy from either of the guidepost values would immediately suggest the intervention of some new feature of mechanism. In contrast, as Salomaa has commented, it is difficult to detect the incursion of the competing "bimolecular" mechanism from inspection of the plot of log k_ψ versus $-H_0$. This example illustrates the sensitivity of the new procedure.

Classification According to w^*-Values.—Instead of $-H_0$, one may use log[HX] as a measure of acidity. It is reasonable to inquire whether plots of (log k_ψ − log[HX]) against log a_{H_2O} might also be linear. In fact, they sometimes are. Figure 6 is an example. The slope in such a plot is taken to define another parameter, w^*, which is an alternative representation of the response of the reaction to catalysis by strong acids.[85]

Reactions which give somewhat curved plots of (log k_ψ + H_0) often give straight plots of (log k_ψ − log[HX]) against log a_{H_2O}; see Fig. 6 for example. In such cases w^* is a more precise index of the response of the reaction to catalysis by concentrated acids since it is less dependent on the range of acid concentrations used; w^* is thus a valuable complementary parameter.

With respect to reactions in sulfuric acid, a difficulty in determination of w^*-values is that the extent of acid dissociation of bisulfate ion in the region of perhaps 0.5–3 M is not known. This difficulty can be circumvented in two ways. One is to base determination of w^* on measurements only at higher sulfuric acid concentrations, say above 4 M. The other, which I have used, is to use rate coefficients for some reaction with a high w-value as a tertiary measure of acidity. I have used Zucker and Hammett's data on rates of iodination (enolization) of acetophenone in sulfuric acid[3] for this purpose. Plotting (log k_ψ − log k_A) against log a_{H_2O} often gives a straight line, the slope of which defines a third parameter,

(84) P. Salomaa, Acta Chem. Scand., **11**, 239 (1957); P. Salomaa and R. Linnantie, ibid., **12**, 2051 (1958).

(85) With moderately basic or strongly basic substrates, one plots, respectively, {log k_ψ − log{[HX]/(h_0 + K_{SH^+})}} or (log k_ψ − log [HX] − H_0) versus log a_{H_2O} in order to define w^*-values.
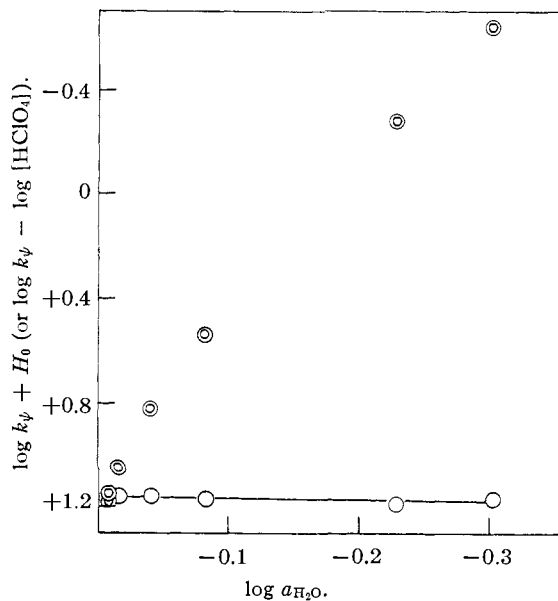
Fig. 6.—Hydrolysis of α-glyceryl monobenzoate in perchloric acid solutions. Plots of log k_ψ − log [HClO$_4$] (open circles) and log k_ψ + H_0 (bulls-eyes) against log a_{H_2O}. The slopes, w^* and w, are -0.1 and $+6.1$, respectively; reaction 68, Table I.

w_a. (Log k_A is the logarithm of the rate coefficient for acetophenone enolization at the same sulfuric acid concentration, as interpolated from the data of Zucker and Hammett.[3]) Since acetophenone enolization in perchloric acid and acetone enolization in hydrochloric acid have w^*-values of -1.62 and -1.66, respectively, a rough conversion of w_a to w^* may be made subtracting 1.6. When this transformation is applied to two ester hydrolyses in sulfuric acid (reactions 62b and 65b), the resulting w^*-values (-0.5 and -0.2, respectively) are similar to those for hydrolysis of the same esters in hydrochloric acid.

w^*- or w_a-values have been computed for all reactions in Table I with $w > +3$, and are listed in the right-hand part of the table.

A notable feature of many plots of (log k_ψ + H_0) against log a_{H_2O} for carboxylic ester hydrolyses is their arrow straightness over a very broad range of acid concentrations; reactions 62a, 63, 65a, 71 and 72 merit particular attention. It is interesting that plots of (log k_ψ − log[HX]) against log a_{H_2O} for these same reactions all are curved; the slope (negative) is considerable at low acid concentrations, but the curve gradually flattens as acid concentration increases. These reactions, unlike most of high w-value, show variation of w^* with acid concentration. What mechanistic significance may this have?

Relationship of w^*- to w-Values.—If plots of (log k_ψ + H_0) and of (log k_ψ − log [HX]) against log a_{H_2O} are linear, the equations

$$\log k_\psi + H_0 = w \log a_{H_2O} + C$$

and

$$\log k_\psi - \log[HX] = w^* \log a_{H_2O} + C'$$

are implied. Subtraction of the second from the first gives
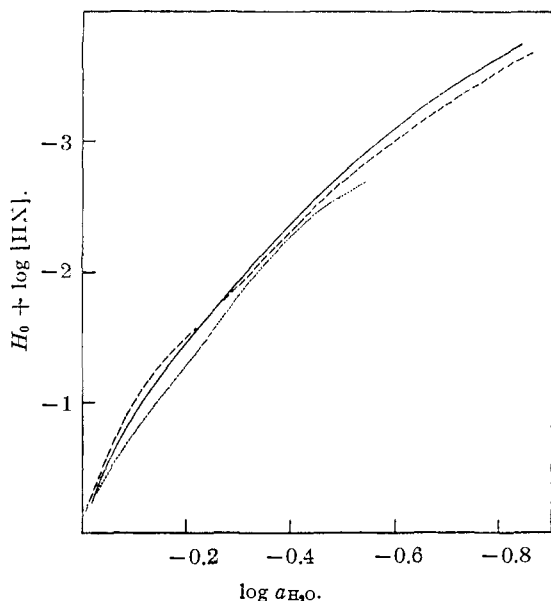
$$H_0 + \log[HX] = (w - w^*) \log a_{H_2O} + C''$$

Fig. 7.—The difference between $-H_0$ and log [HX] as a function of log a_{H_2O}: solid line, HClO$_4$; dashed line, H$_2$SO$_4$; dotted line, HCl.

A plot of $(H_0 + \log[\mathrm{HX}])$ against log a_{H_2O} should then be linear. Plots of this sort for hydrochloric, sulfuric and perchloric acids are presented in Fig. 7. They do approximate linearity, but there is a clear tendency toward curvature over broad ranges of acid concentration. The curves for hydrochloric and perchloric acids are simpler to consider because the complication of an incomplete second dissociation is absent. These two show a steep initial portion of slope about $+10$, then a truly straight middle portion and finally a tail of steadily decreasing slope. The straight middle portion is longest in the case of hydrochloric acid; it extends from 3.5 M to 7.5 M with slope $+5.3$. The slope is $+2.4$ between 9.5 M and 10 M. In the case of perchloric acid, the straight middle portion covers the range 4.5 M to 7.0 M and has slope $+4.5$; the final slope (9.0 to 9.5 M) is $+2.0$. The sulfuric acid curve has a straight portion covering the range 3.5 to 7.0 M with slope $+4.3$; the final slope (9.5 to 10.0 M) is $+2.0$.

In view of the curvature in these plots, it is not to be expected that plots of both $(\log k_\psi + H_0)$ and of $(\log k_\psi - \log[\mathrm{HX}])$ against log a_{H_2O} will be truly linear over a long range of acid concentrations. If one is straight, the other must be somewhat curved corresponding to the changes in slope in Fig. 7. However, if data from the middle range where the lines are really straight are considered, it is possible that both types of plots may be accurately linear; if so, $(w - w^*)$ will have the values 5.3, 4.3 and 4.5 in hydrochloric, sulfuric and perchloric acids, respectively.

Relations of w and w^* to the H_0 Scale.—The H_0 or h_0 acidity function appears in the expressions used in computation of w-values for weakly basic substrates, and of w^* for strongly basic, and of both parameters to varying extents for moderately basic substrates. This stems from the assumption made that protonation of substrates is accurately

represented by the H_0 function. Any fault in this assumption with respect to a particular substrate, or any deficiency in the H_0 scales of Paul and Long,[86] will be reflected in the relevant w- or w^*-values. w^* for weakly basic and w for strongly basic substrates are independent of the H_0 scale.

Use of w^* as a primary classification parameter for the great majority of substrates which are weakly basic might therefore seem preferable. However, the prevalence of curvature in w^* plots, except when w^* is within a couple of units of zero (i.e., w rather high), makes the majority of w^*-values dependent on the acid concentration range studied. It is this practical consideration which favors w as the principal parameter.

Recommendations.—It is recommended that reactions occurring in mineral acids more concentrated than 1 M be classified primarily according to their w-values. w is defined as the slope in a plot of $(\log k_\psi + H_0)$, $\{\log k_\psi - \log[h_0/(h_0 + K_{\mathrm{SH^+}})]\}$ or log k_ψ (as appropriate) against log a_{H_2O}. When there is appreciable curvature in the aforesaid plots and/or when w exceeds $+3.0$, it is recommended that the w^*-value be cited as a complementary index parameter. w^* is defined as the slope in a plot of $(\log k_\psi - \log[\mathrm{HX}])$, $\{\log k_\psi - \log\{[\mathrm{HX}]/(h_0 + K_{\mathrm{SH^+}})\}$ or $(\log k_\psi - \log[\mathrm{HX}] - H_0)$ against log a_{H_2O}, with the exception that these expressions should not be used with respect to sulfuric acid less than 3.5 M. When the plots used to define w are appreciably curved, fine distinctions should be made between w^*- rather than w-values. For reactions occurring in sulfuric acid below 3.5 M, the w_a parameter may be determined from the slope of a plot of $(\log k_\psi - \log k_A)$ versus log a_{H_2O}; w_a may be converted roughly into w^*-values by subtracting 1.6.

It is recommended that the Zucker–Hammett categories of correlation with $-H_0$ or with log [HX] not be used for serious classification of reaction because many reactions do not fit these categories and such classification obscures subtle differences between reactions.

Appendix

Principles Used in Selection of Data for Scrutiny.—All reactions occurring in aqueous hydrochloric, sulfuric, perchloric and nitric acids have been scrutinized, insofar as they came to my attention before Oct. 1, 1960. Data in the following categories have been excluded: (a) data at mineral acid concentrations less than 0.5 M; (b) data for media containing more than 5% of an organic solvent component or of the substrate; (c) data known to be faulty or pertaining to reactions in which there is a known complication involving the anion of the mineral acid (e.g., hydrolysis of nitriles[74,87] or of dialkyl sulfites[53] in hydrochloric acid); (d) data to which an unusual correction factor must be applied (e.g., the hydration of olefins[88]);

(86) M. A. Paul and F. A. Long, Chem. Revs., 57, 1 (1957).

(87) M. L. Kilpatrick, J. Am. Chem. Soc., 69, 40 (1947).

(88) R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, ibid., 77, 1584 (1955).

(e) sets of data comprising fewer than three rate coefficients or lacking rate coefficients for greater than 2 M acid concentration; and (f) certain early data which are superseded by later and more comprehensive data on the same reaction. Data for reactions in concentrated sulfuric acid ($> 10\ M$) have been included occasionally but not systematically.

K_{SH^+}-Values for Substrates of Intermediate Basicity.— K_{SH^+} appears in the functions plotted for determination of w or w^*. In several cases (reactions 32, 57, 58 and 85) acceptable linear plots were obtained with use of K_{SH^+} values reported in the literature. In two reactions (34 and 41), definitely curved plots were obtained when published K_{SH^+}-values were used but good linear plots resulted when other K_{SH^+}-values were employed. Inspection of the data (insofar as available) underlying the published values suggested they might be wrong, and so the values which gave the best straight lines were used in constructing Table I.[89] For reactions 33, 36, 37 and 70, no determinations of K_{SH^+} were found in the literature; values which gave good straight lines were used.

Acetone (reaction 76) was treated as a very weak base. Its pK_{SH^+} has recently[91] been determined to be -7.2; the pK_{SH^+} of -1.58[92] used by Archer and Bell[69] is incorrect.

Values for H_0 and for the Activity of Water.—H_0-Values interpolated from the tables of Paul and Long[86] were used throughout; other H_0 values tabulated with experimental data by some authors were disregarded. Activity of water data from various literature sources were used. Most a_{H_2O} values are recorded in the literature as a function of *molality*, and conversion to the *molarity* scale required tedious calculation taking densities into account. Plots of log a_{H_2O} against acid molarity were constructed, and log a_{H_2O} values were read off the smoothed curves. For the convenience of other workers, log a_{H_2O} values for three common acids at 0.5 M intervals, as read off my plots, are given in Table II.

For sulfuric acid, especially the more concentrated solutions, many authors represent concentration by weight per cent. It was therefore convenient to construct auxiliary plots of log a_{H_2O} *versus* percentage sulfuric acid, using the values of Shankman and Gordon[93] below 69% and of Deno and Taft[94] above 69%.

Reactions Giving Irregular Plots by the New Procedure.— *Hydrolysis of acetic anhydride*[95]: In 0.8–5.8 M HClO₄, the plot of (log $k_\psi + H_0$) *versus* log a_{H_2O} is straight with nearly zero slope (w -0.45, σ_w 0.41, σ_y 0.02 and r 0.361) below 2.6 M and w -0.38, σ_w 0.27, σ_y 0.06 and r 0.421 above 2.6 M), but in 4.6–9.3 M HCl and in 0.7–7.4 M H₂SO₄ plots of the same sort are sharply bent; initial steep slopes (*ca.* $+12$ in 0.7–1.6 M H₂SO₄, $+3.9$ in 4.6–5.6 M HCl) change rather sharply to near zero slopes at higher concentrations. *Hydration of acrylonitrile to acrylamide*[96]: In 26–85% H₂SO₄, a plot of (log $k_\psi + H_0$) *versus* log a_{H_2O} curves sharply downward; the initial slope of $+2.2$ flattens to a final slope of $+0.4$. The plot of {log k_ψ — log [$h_0/(h_0 + K_{SH^+})$]} *versus* log a_{H_2O}, which should be used if K_{SH^+} of 20,000 as given by Lemaire and Lucas[89] for acetonitrile is applicable, is U-shaped. *Hydrolysis of phthalamic acid*:[97]

(89) Preliminary measurements in this Laboratory by Miss Elisabeth Moraillon, who used the method of Lemaire and Lucas,[90] support the K_{SH^+} values for benzamide and acetylglycine used in constructing Table I.

(90) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5198 (1951).

(91) H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960).

(92) S. Nagakura, A. Minegishi and K. Stanfield, *J. Am. Chem. Soc.*, **79**, 1033 (1957).

(93) S. Shankman and A. R. Gordon, *J. Am. Chem. Soc.*, **61**, 2370 (1939).

(94) N. C. Deno and R. W. Taft, Jr., *ibid.*, **76**, 244 (1954).

(95) V. Gold and J. Hilton, *J. Chem. Soc.*, 838, 843 (1955).

(96) N. C. Deno, T. Edwards and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2108 (1957).

Molarity	HCl	—log a_{H_2O} H₂SO₄	HClO₄
0.5	-0.008	-0.008	-0.008
1.0	$-$ .017	$-$ .018	$-$ .018
1.5	$-$ .027	$-$ .030	$-$ .030
2.0	$-$ .039	$-$ .043	$-$ .043
2.5	$-$ .053	$-$ .063	$-$ .060
3.0	$-$ .070	$-$ .085	$-$ .081
3.5	$-$ .087	$-$ .111	$-$ .106
4.0	$-$ .107	$-$ .142	$-$ .135
4.5	$-$ .130	$-$ .176	$-$ .172
5.0	$-$ .155	$-$ .219	$-$ .215
5.5	$-$ .181	$-$ .267	$-$ .271
6.0	$-$ .211	$-$ .320	$-$ .330
6.5	$-$ .244	$-$ .377	$-$ .411
7.0	$-$ .279	$-$ .439	$-$ .496
7.5	$-$ .318	$-$ .510	$-$ .602
8.0	$-$ .358	$-$ .587	$-$ .714
8.5	$-$ .399	$-$ .670	$-$ .842
9.0	$-$ .444	$-$ .761	$-$ .983
9.5	$-$ .490	$-$ .859	-1.150
10.0	$-$ .539	$-$ .968	.....
10.5	$-$ .591	-1.082	.....

In 1.0–10.0 M HCl, the plot of {log k_ψ — log [$h_0/(h_0 + K_{SH^+})$]} *versus* log a_{H_2O} shows pronounced downward curvature using the published K_{SH^+} of 316; the plot could not be made to straighten by using other K_{SH^+} values. *Hydrolysis of o-nitrophenyl hydrogen oxalate*.[98] A J-shaped plot of {log k_ψ — log [$h_0/(h_0 + K_{SH^+})$]} *versus* log a_{H_2O} was obtained using the published K_{SH^+} of 0.35; a fair approximation to a straight line of slope $+4.7$ was obtained using K_{SH^+} 4.5, but this value seems incompatible with other observations of Bender and Chow.[98] *Deoxymercuration of β-2-methoxycyclohexylmercuric iodide*[99]: Plots of (log $k_\psi + H_0$) *versus* log a_{H_2O} in 1.8–5.6 M H₂SO₄ and 1.1–4.6 M HClO₄ show no semblance of linearity. *Decarbonylation of 2,4,6-trimethoxybenzaldehyde*[100]: Based on the published K_{SH^+} of 130, a plot of {log k_ψ–log [$h_0/(h_0 + K_{SH^+})$]} *versus* log a_{H_2O} for reaction in hydrochloric acid was approximately linear with slope about $+0.9$. However, the corresponding plot for perchloric acid was curved. The perchloric acid data gave a linear plot (slope about $+1.9$) when a K_{SH^+} of 26 was used, but the corresponding plot for hydrochloric acid was gently U-shaped.

(97) M. L. Bender, Y.-L. Chow and F. Chloupek, *ibid.*, **80**, 5380 (1958).

(98) M. L. Bender and Y.-L. Chow, *ibid.*, **81**, 3929 (1959).

(99) M. M. Kreevoy and F. R. Kowitt, *J. Am. Chem. Soc.*, **82**, 739 (1960).

(100) H. Burkett, W. M. Schubert, F. Schultz, R. B. Murphy and R. Talbott, *ibid.*, **81**, 3923 (1959).