rather regularly with increase of initial concentration of hydrochloric acid at all temperatures, as we pass from solution C to B to A. Since the activity of the acid is greater at the beginning than at the end of the reaction the individual coefficients from the time method in any given solution tend to be greater as the reaction proceeds. Consequently the mean coefficients decrease as the temperature is raised.

If the reaction velocity constants which have been determined by use of the empirical equation be plotted, log K against $1/T$ (Fig. 4), in conformance with the differential form of the Arrhenius equation, $d \ln k/dT = Q/RT^2$, a straight line is obtained for each of the solutions.

Moreover, from the integral form of this same equation

$$\ln \frac{k_1}{k_2} = \frac{Q}{R}\,\frac{T_1 - T_2}{T_1T_2}$$

values for Q at fifteen degree intervals may be calculated. The values thus obtained are within the usual limits of constancy.

Summary

1. New data are presented for the velocity of conversion of pyrophosphate to orthophosphate in aqueous solution in the presence of three different concentrations of hydrochloric acid at five temperatures, 30, 45, 60, 75 and 90°. $Na_4P_2O_7 \cdot 10H_2O$ was used.

2. An empirical equation for the velocity of the reaction has been developed.

3. Temperature coefficients for 15° intervals have been calculated.

4. The values for Q in the equation of Arrhenius are within the usual limits of constancy.

5. A modification of the method for the quantitative determination of pyrophosphate in presence of orthophosphate by use of zinc acetate has been made.

NEW YORK, N. Y. RECEIVED AUGUST 3, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Relative Strengths of Acids in *n*-Butyl Alcohol[1]

BY LELAND A. WOOTEN AND LOUIS P. HAMMETT

We have measured the relative strengths of a series of substituted carboxylic and phenolic acids in *n*-butyl alcohol, a hydroxylic solvent of relatively low dielectric constant, and have found certain relationships between the structure of the acid and the effect upon the relative strength of the transfer of the acid from water to this solvent. The solubility of lithium chloride in this solvent made it possible to work in a medium of high and constant strength, a necessary condition for the measurement of relative acid strength by the potentiometric method if specific salt effects are to be minimized or eliminated and the uncertainty due to liquid junction potentials avoided. Butylate ion was employed as the base.

Experimental

Method.—Concentration cells of the following type were set up and measured

$$\text{Au}\left|\begin{array}{c}\dfrac{\text{HA}_1}{\text{NaA}_1}=1\\ \text{LiCl, }0.05\ M\\ \text{Quinhydrone}\end{array}\right\|_{a}\begin{array}{c}\text{Satd. soln.}\\ \text{of LiCl}\end{array}\Big\|_{b}\begin{array}{c}\dfrac{\text{HA}_2}{\text{NaA}_2}=1\\ \text{LiCl, }0.05\ M\\ \text{Quinhydrone}\end{array}\Big|\,\text{Au}$$

The electromotive force of this cell at 25° is related to the relative strength of the two acids, HA_1 and HA_2, by the expression

$$\text{E. m. f.}/0.0591 = pK_2 - pK_1 = \Delta pK$$

where $pK = -\log K$, the negative logarithm of the ionization constant of the acid. This expression is a sufficiently precise approximation provided the acids exhibit normal weak-acid titration curves in the solvent under study. Since a fairly high neutral salt concentration (LiCl) was maintained throughout the whole system the junction potentials at *a* and *b* should be small and practically constant.

The cell used was essentially that employed by Hammett and Dietz.[2] Mixing of the solutions was minimized by ground glass plugs, which separated the buffer solutions from the salt bridge. The buffer solutions were approximately 0.0025 M and in all cases were made 0.05 M with respect

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[1] Dissertation submitted by Leland A. Wooten to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1935. The material was presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Hammett and Dietz, THIS JOURNAL, **52**, 4795 (1930).

to lithium chloride. The measurements were made in an atmosphere of dry nitrogen. Rubber stoppers carried the electrodes as well as inlets and outlets for the nitrogen. A trap on the nitrogen outlet, containing *n*-butyl alcohol, sealed the system from the atmosphere. All measurements were made at room temperature, which was 25 ± 3°.

Apparatus

Potentiometer System.—The voltages were measured with a Leeds and Northrup Type K potentiometer in conjunction with a No. 2500-b Type R wall galvanometer of the same make. A newly calibrated Weston Standard cell was used in standardizing the working circuit. This system applied to butyl alcohol solutions permitted voltages to be measured to ±0.1 millivolt.

Electrodes.—In agreement with other workers, notably Hammett and Dietz[2] and Halford,[3] it was found that bright platinum is not a satisfactory electrode material for the quinhydrone reaction in non-aqueous solution. Electrodes made from new C. P. platinum wire, when first used, gave reliable results in *n*-butyl alcohol solution; after some use, however, they became erratic in behavior, disagreeing among themselves and with former measurements on the same buffer. No method of cleaning could be depended upon to restore their original good characteristics. Old platinum wire electrodes which had been used previously in inorganic oxidation–reduction systems in aqueous solution were always very erratic. These observations support the hypothesis of Hammett and Dietz[2] that platinum readily picks up surface impurities which are electromotively active, thus causing variations in the electrode potentials.

Gold-on-glass electrodes similar to those used by Hammett and Dietz[2] were prepared by the method of Newberry[4] except that the gold was deposited from a solution of gold trichloride in *n*-butyl alcohol instead of in ethyl alcohol. They were found to give satisfactory results in *n*-butyl alcohol solution provided they were subjected to a preheating treatment immediately before use. This treatment consisted in washing with ethyl alcohol, heating to dull redness in the tip of a Bunsen flame, and finally cooling in air. When treated by this method immediately before immersion in the solution to be measured, individual electrodes seldom failed to agree with each other within 1 millivolt and usually agreed within a few tenths of a millivolt.

After some use, however, gold-on-glass electrodes sometimes failed to give reproducible values when first immersed in the solution to be measured, even though they had been subjected to the usual heat treatment. In these cases the electrodes would finally attain a reproducible value, but the rate of attainment of equilibrium was very slow. This indicates that the catalytic properties of the electrode change with use. It is possible that as the electrode is used surface impurities are picked up (as in the case of platinum), which either lower the activity of the catalyst, or as a result of a lowered activity of the catalyst, become predominant in their effect on the electrode potential.

Three pairs of electrodes were used in all cells. Criteria of reliability of electrodes were: (1) agreement between several electrodes in the same buffer; (2) rapid attainment of equilibrium; and (3) in later work the reproducibility of the voltage of a given cell. The salicylate–benzoate cell was used many times for this purpose.

In addition to the electrode trouble described above there was observed at times a very slow drift in the potential of the cell being measured. That this drift was the result of a real change in the quinhydrone equilibrium was indicated by the fact that it occurred when all the electrodes were in close agreement. The rate of drift was greater as the buffer solution was made more alkaline and was generally in the direction of reduction of quinone rather than of oxidation of hydroquinone. It was found that in one or two cases the rate of drift was greatly reduced by passing the nitrogen over rather than through the solution, but this behavior could not be reproduced. As a result of these observations, however, the nitrogen was passed through the solutions only for fifteen to twenty minutes initially when the cell was set up, after which it was passed over the solution for the remainder of the period of test. This procedure seemed to give somewhat steadier potentials.

Colorimeter.—A Klett–Beaver comparator was used in the colorimetric work.

Materials

***n*-Butyl Alcohol.**—The Eastman product listed as practical (Cat. No. P-50) was used throughout this work. It was purified by extended treatment with anhydrous barium oxide, followed by distillation from barium oxide at reduced pressure (30 to 40 mm. of mercury) in an all-Pyrex glass distillation apparatus. This apparatus was fitted with a Widmer fractionating column 30 cm. in length. The presence of an excess of porous lumps of the anhydrous barium oxide permitted the distillations to be carried out at low pressure without the introduction of air or gas usually admitted to prevent bumping. The product was acid and aldehyde free. The boiling point was 117 ± 1°. The dielectric constant[5] of the purified solvent was 17.4 ± 0.1 at 24.5° when measured at frequencies of 10 and 100 k.c.

After use, the solvent was re-purified by subjecting it to two or more vacuum distillations as described above, after which it could again be used.

The Alkali Reagent.—A solution of 0.1 *N* sodium butylate was prepared by the interaction of metallic sodium and pure *n*-butyl alcohol. Before adding the sodium, the alcohol was saturated with hydrogen or nitrogen to displace carbon dioxide. After preparation, the solution was immediately stored under hydrogen in a Pyrex bottle made light-proof by painting with black lacquer. The bottle was fitted with a stopper which carried two tubes; one of these was connected through a drying tower to a tank of compressed hydrogen, and the other, which extended nearly to the bottom of the bottle, was connected to a three-way stopcock buret of 10-ml. capacity. The open end of the buret was fitted with a soda-lime tube. Before filling, the air in the buret was swept out by passing through it a stream of hydrogen. It was filled by means of a slight pressure from the compressed hydrogen tank.

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(3) Halford, THIS JOURNAL **53**, 2944 (1931); *ibid.*, **55**, 2272 (1933).

(4) Newberry, *Trans. Electrochem. Soc.*, **64**, 209 (1933).

(5) The dielectric constant was measured by Dr. S. O. Morgan.

An alkali solution thus prepared and stored usually remained constant in titer against standard benzoic acid for at least one month.[6] Its purity was frequently tested by titrating potentiometrically portions of a standard picric acid in butyl alcohol solution, according to the method described by Wooten and Ruehle,[6] which provides a sensitive test for the presence of weak acid salts.

Since lithium chloride was to be added to the solutions under study, an attempt was made to employ lithium butylate as the alkali reagent, thus simplifying the system by limiting it to lithium salts. It was found, however, that lithium butylate is almost completely insoluble in butyl alcohol.

Lithium Chloride.—This salt was obtained from two sources. The fused product from Kahlbaum was found to contain 0.3% free alkali. This proved so troublesome to purify that its use was abandoned for a special anhydrous product obtained from Merck and Company which was practically free from alkali and could be used without further purification. Saturated solutions were prepared by heating in a Pyrex glass reflux apparatus a portion of the pure solvent in contact with an excess of the anhydrous salt. The solutions of lithium chloride in butyl alcohol obtained by this method were approximately 2.1 *M* when allowed to come to equilibrium at room temperature.

Quinhydrone.—The quinhydrone used in most of the work was obtained from the Eastman Kodak Co., melting point 170°. Recrystallization from butyl alcohol did not perceptibly improve its quality.

Owing to its high solubility in *n*-butyl alcohol it was not feasible to employ a saturated solution of quinhydrone. Consequently it was added in equivalent quantities to each half cell in concentration of 50 mg. per 100 ml. of solution. Variation of the concentration of quinhydrone did not influence the voltage of the cell.

Compressed Nitrogen.—Tank nitrogen was purified by passing it through towers containing soda-lime and phosphorus pentoxide and through a fritted glass wash bottle containing *n*-butyl alcohol, which served to saturate the gas with alcohol vapor. No attempt was made to remove the small amount of oxygen known to be present.

Acids.—With the exception of benzoic and trimethylbenzoic, the acids used were obtained from the Eastman Kodak Company. The benzoic acid was the Bureau of Standards Alkalimetric Standard No. 39d, and was employed both as a primary alkalimetric standard and as a standard in the measurement of relative strength. Trimethylbenzoic acid was prepared from bromomesitylene by the method of Bamford and Simonsen.[7,8]

Solid acids were dried in an oven at suitable temperature and stored over phosphorus pentoxide. In some cases they were further purified as indicated in the following table. In general they were considered of sufficient purity if they gave correct melting points within ±1°. Liquid acids were dried by treatment with anhydrous sodium sulfate followed by distillation at reduced pressure, and characterized by their boiling points. An additional check on the purity of the acids was the determination of the equivalent weight by titration in butyl alcohol with standard sodium butylate solution. The analytical results obtained on the acids are listed in Table I.

TABLE I

Acid	Physical constants, m. p., °C.	Analyses, %	Remarks
Benzoic	121.5		
o-Chlorobenzoic	141	99.7	Recryst. from alc.
m-Chlorobenzoic	154	99.7	Recryst. from water
p-Chlorobenzoic	240–241	99.9	Sublimed
o-Nitrobenzoic	147	99.8	Recryst. from hot water
m-Nitrobenzoic	142	99.6	
p-Nitrobenzoic	241–242	99.7	
o-Toluic	102	99.8	
m-Toluic	111–112	99.8	Recryst. from alc.
p-Toluic	177–178	99.7	
o-Methoxybenzoic	102–103	99.6	Recryst. from hot water
Anisic	184–185	99.8	Recryst. from alc.
Salicylic	158	100.0	Recryst. from alc.
Trimethylbenzoic	152–153	99.9	Recryst. from hot CCl_4
Formic	B. p. 100	99.8	
Acetic	B. p. 118	99.9	
Chloroacetic	61–62	99.6	
Dichloroacetic	B. p. 194	99.5	
Trichloroacetic	57	98.0	
Propionic[a]	B. p. 141.3		
α-Chloropropionic	B. p. 186	100.5	
β-Chloropropionic	42	99.8	
Butyric[a]	B. p. 163.3		
n-Valeric[a]	B. p. 186.6		
n-Caproic[a]	B. p. 202		
n-Caprylic	B. p. 237		
Maleic	138	99.7	
d-Camphoric	181	99.7	
p-Nitrophenol	114	99.7	
2,4-Dinitrophenol	112	99.6	
Picric	121	99.6	

[a] Purified by Mr. H. Wadlow. These acids were treated with anhydrous sodium sulfate and triple distilled at low pressure in a special distillation apparatus.

Precision and Reliability

Logarithmic titration curves were employed to demonstrate that the acids studied behave as normal weak acids in *n*-butyl alcohol solutions of high and constant ionic strength. Some of these curves are shown in Figs. 1 and 2. Excluding picric and trichloroacetic acids, which are moderately strong acids even in *n*-butyl alcohol, the average slope of the curves obtained is 58 ± 2 millivolts per logarithmic unit, which is in close agreement with the theoretical slope given by

$$\Delta E/\Delta \log \frac{X}{1 - X} = 59 \text{ mv. at } 25°$$

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[6] Wooten and Ruehle, *Ind. Eng. Chem., Anal. Ed.*, **6**, 449 (1934).

[7] Bamford and Simonsen, *J. Chem. Soc.*, **97**, 1906 (1910).

[8] This acid was prepared and purified by Mr. H. P. Treffers.

where X is the fraction neutralized at voltage E.

Table II shows typical data obtained on two representative cells. Three pairs of electrodes were used in each buffer.

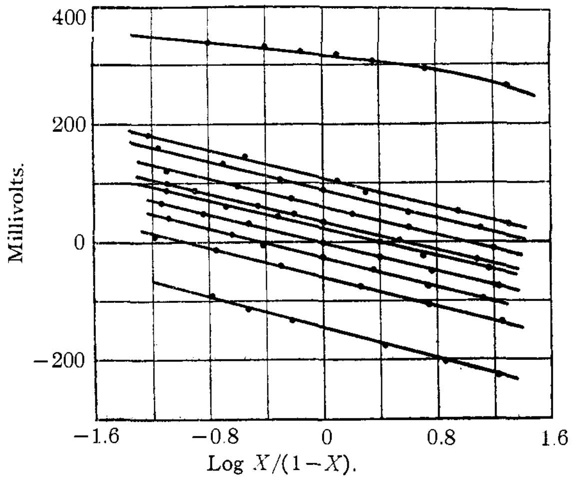

Fig. 1.—Logarithmic titration curves with quinhydrone electrode in *n*-butyl alcohol, 0.002 M acids titrated with 0.1 M sodium butoxide: in order, from the top, picric, 2,4-dinitrophenol, salicylic, *o*-chlorobenzoic, *m*-chlorobenzoic, *p*-chlorobenzoic, benzoic, *p*-methoxybenzoic, trimethylacetic, *p*-nitrophenol.

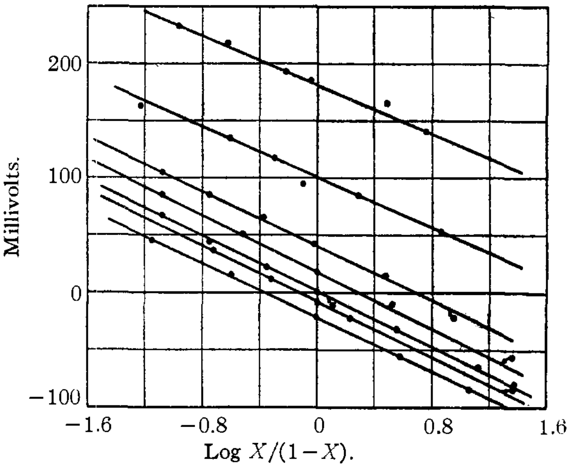

Fig. 2.—Logarithmic titration curves with quinhydrone electrode in *n*-butyl alcohol, 0.002 M acids titrated with 0.1 M sodium butoxide: in order from the top, dichloroacetic, chloroacetic, trimethylbenzoic, *o*-methoxybenzoic, *o*-toluic, *p*-toluic, *n*-caprylic.

TABLE II

(a) Salicylate–Benzoate Cell

Time	E_1, mv.	E_2, mv.	E_3, mv.
10 min.	88.9	91.3	90.8
15 min.	88.9	90.5	90.0
2 hrs.	89.0	90.6	90.5
20 hrs.	91.6	91.5	91.1

(b) Butyrate–Benzoate Cell

Time	E_1, mv.	E_2, mv.	E_3, mv.
10 min.	19.4	20.0	20.0
30 min.	21.1	20.7	20.7
45 min.	20.9	20.8	20.8
3 hrs.	21.0	20.9	21.0

Table III shows the reproducibility of the method. The values shown were obtained on salicylate–benzoate cells prepared at different times from different reagents. The measurements were made under the same conditions except for small variations in room temperature. Each value is the average of a number of measurements using three electrode pairs over a period of at least two hours.

From the results presented in Tables II and III it is seen that the precision limits of the method are easily within ±0.05 logarithmic units.

TABLE III

SALICYLATE–BENZOATE CELL

Date	E, mv.	Dev. from mean
5/19/34	88.5	−0.4
5/27/34	86.0	−2.9
6/4/34	86.3	−2.6
9/20/34	91.0	+2.1
10/6/34	90.2	+1.3
10/7/34	90.0	+1.1
11/7/34	88.5	−0.4
12/31/34	91.3	+2.4
	Average 88.9	±1.6

Effect of Water.—Although precautions were taken to dry the solvent, acids and other reagents before use, the method employed did not permit the measurements to be made without some exposure of the solutions to the atmosphere. It was therefore necessary to determine the influence of water upon the electromotive force of a typical cell. In the following table the effect of water upon the salicylate–benzoate cell is shown. The same effect was observed on a number of different cells.

TABLE IV

Per cent. water added		E. m. f.	
Benzoate arm	Salicylate arm	E_1	E_2
0.0	0.0	90.1	90.1
.1	.0	91.2	91.3
.5	.0	94.5	94.6
1.0	.0	98.8	98.2
2.0	.0	101.5	101.0
3.0	.0	104.7	104.5
5.0	.0	109.5	109.0
5.0	5.0	91.3	91.0

These results show that water has definite basic properties in *n*-butyl alcohol solution and thus causes a decrease in the potential of the half-cell to which it is added. But if it is present in equivalent quantities in both half cells the effect on the voltage of the cell is apparently negligible. Traces of moisture in the solvent therefore should not alter the relative strength of the acids. The linearity of the logarithmic titration curves, however, indicates that the solvent was comparatively free of moisture.

Effect of Varying Neutral Salt.—To determine whether an 0.05 *M* concentration of lithium chloride was sufficient to produce a sensibly constant ionic environment when working with 0.0025 *M* buffer solutions the following experiment was carried out.

TABLE V

EFFECT OF VARYING NEUTRAL SALT CONCENTRATION ON THE SALICYLATE–BENZOATE CELL

Molar salt concentration		E. m. f.	
Salicylate arm	Benzoate arm	E_1	E_2
0.00	0.00	121.2	120.8
.00	.05	77.0	77.5
.05	.05	90.1	90.3
.05	.10	84.4	84.1
.10	.10	90.2	89.5
.10	.15	86.4	86.5
.15	.15	90.6	90.9

The results shown in Table V indicate that as the salt concentration is increased the voltage of the cell becomes less sensitive to changes in salt concentration. Beyond 0.05 *M*, large variations in salt concentration may occur without greatly influencing the electromotive force of the cell. The agreement of the logarithmic titration curves with the theoretical slope (Figs. 1 and 2) also indicates that an 0.05 *M* salt concentration is sufficient to produce a sensibly constant ionic environment when the concentration of the acid is 0.002 to 0.003 *M*.

Effect of Temperature.—Tests on the salicylate–benzoate and acetate–benzoate cells showed that a change in temperature of 10° caused a change in voltage of approximately 2 millivolts. It was concluded from these tests that the error caused by variations in temperature of ±3° was negligible compared to other sources of error in the method.

Results

The results on the relative strengths of acids obtained by the potentiometric method are summarized in Table VI. Variations in relative strength are expressed in logarithmic units. A negative sign indicates that an increase in acid strength relative to benzoic acid occurs when the acid is transferred from water to butyl alcohol, a positive sign that a decrease occurs.

The values for $pK_{\mathrm{H_2O}}$ in Table VI are at 25° and are from Landolt–Börnstein "Tabellen" unless otherwise indicated.

TABLE VI

Acid	$pK_{\mathrm{H_2O}}$	$\Delta pK_{\mathrm{H_2O}}$	$\Delta pK_{\mathrm{BuOH}}$	Change in relative strength
Benzoic	4.20[9]	0	0	0
o-Chlorobenzoic	2.92[9]	−1.28	−1.00	+0.28
m-Chlorobenzoic	3.82[9]	−0.38	−0.60	− .22
p-Chlorobenzoic	3.96[9]	− .22	− .42	− .20
o-Nitrobenzoic	2.19	−2.01	−1.74	+ .27
m-Nitrobenzoic	3.46	−0.74	−1.09	− .35
p-Nitrobenzoic	3.40	− .80	−1.12	− .32
o-Toluic	3.90	− .30	−0.02	+ .28
m-Toluic	4.25	+ .05	+ .09	+ .04
p-Toluic	4.37	+ .17	+ .21	+ .04
o-Methoxybenzoic	4.08[10]	− .12	− .31	− .19
Anisic	4.48[10]	+ .28	+ .40	+ .12
Salicylic	2.97	−1.25	−1.50	− .27
Trimethylbenzoic	3.43	−0.77	−0.68	+ .09
Formic	3.75[11]	− .45	−1.09	− .64
Acetic	4.76[12]	+ .56	+0.05	− .51
Monochloroacetic	2.86[13]	−1.34	−1.71	− .37
Dichloroacetic	1.3	−2.9	−3.1	− .2
Trichloroacetic	0.7	−3.5	−4.1	− .6
Trimethylacetic	5.01	+0.81	+1.01	+ .20
Propionic	4.85	+ .65	+0.41	− .24
α-Chloropropionic	2.83	−1.37	−1.43	− .06
β-Chloropropionic	4.07	−0.13	−0.49	− .36
Butyric	4.83	+ .63	+ .36	− .27
n-Valeric	4.80	+ .60	+ .40	− .20
n-Caproic	4.85	+ .65	+ .39	− .26
n-Caprylic	4.85	+ .65	+ .42	− .23
Maleic (1st)	1.82	−2.38	−3.61	−1.23
Maleic (2d)	6.58	+2.38	+1.96	−0.42
d-Camphoric (1st)	4.37	+0.17	+0.22	+ .05
p-Nitrophenol	7.17	+2.97	+2.41	− .56
2,4-Dinitrophenol	4.10	−0.10	−1.88	−1.78
Picric	0.8	−3.4	−5.4	−2.0

Colorimetric Work.—The relative strengths of 2,4-dinitrophenol and of salicylic, chloroacetic, and *o*-nitrobenzoic acids were determined colorimetrically using 2,4-dinitrophenol as indicator. The strength of the acid (pK_a) is related to the strength of the acid indicator (pK_I) and the degree of dissociation of the indicator (α) in a half-neutralized buffer of the acid in the following way.

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(9) Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934).

(10) "International Critical Tables," Vol. VI.

(11) Harned and Embree, THIS JOURNAL, **56**, 1042 (1934).

(12) Harned and Ehlers, *ibid.*, **55**, 652 (1933).

(13) Wright, *ibid.*, **56**, 314 (1934).

$$pK_a = pK_I + \log \alpha/(1 - \alpha)$$

The buffer solutions were 0.002 molar in acid and salt, the indicator concentration was 0.00004, except for one measurement on the salicylic system, where it was one-half as great. Each item in the tables represents the mean of many colorimetric settings on an individually prepared buffer system. The reference solution for completely ionized dinitrophenol was prepared with sodium butylate in butyl alcohol. The potentiometric values were obtained by the direct comparison of the carboxylic acid with dinitrophenol. They are reasonably consistent with those obtained by comparing both carboxylic acids and dinitrophenol with benzoic acid.

Table VII contains the results obtained in solutions containing 0.05 M lithium chloride as in the potentiometric measurements.

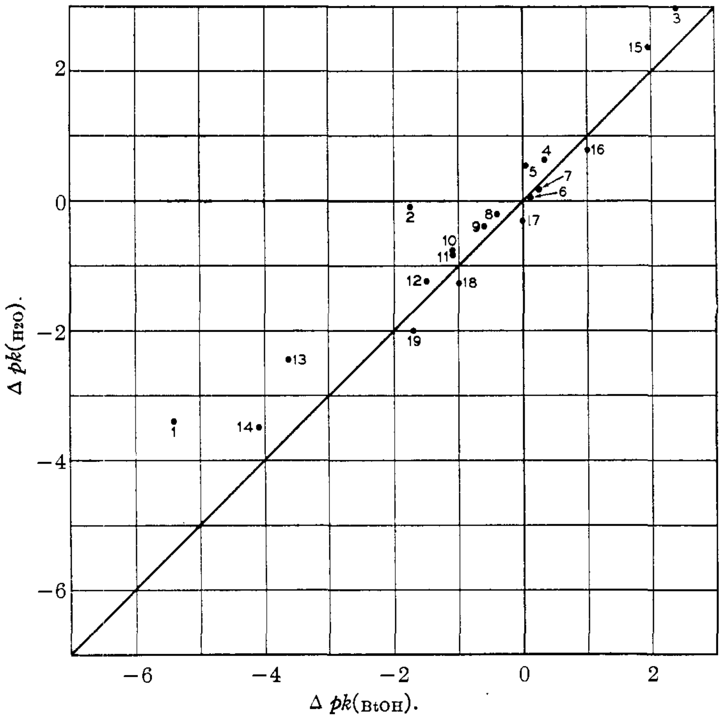

Fig. 3.—Relative strengths of acids in water and in n-butyl alcohol referred to benzoic acid: 1, picric; 2, 2,4-dinitrophenol; 3, p-nitrophenol; 4, butyric; 5, acetic; 6, m-toluic; 7, p-toluic; 8, p-chlorobenzoic; 9, m-chlorobenzoic; 10, m-nitrobenzoic; 11, p-nitrobenzoic; 12, salicylic; 13, maleic (1); 14, trichloroacetic; 15, maleic (2); 16, trimethylacetic; 17, o-toluic; 18, o-chlorobenzoic; 19, o-nitrobenzoic.

TABLE VII

Acid	$pK_a - pK_I$ Colorimetric	Potentiometric
o-Nitrobenzoic	+0.12, 0.08, Av. +0.10	+0.14
Chloroacetic	+0.24	+ .24
Salicylic	+0.55, 0.33, 0.29, 0.22, Av. +0.35	+ .35

The agreement between the potentiometric and the colorimetric work is strong support for the validity of both methods of determining acid strength in this solvent.

Table VIII contains the results of some colorimetric measurements in which no lithium chloride was added.

TABLE VIII

Acid	$pK_a - pK_I$
o-Nitrobenzoic	+0.09, 0.07, 0.27, Av. 0.14
Chloroacetic	+0.21
Salicylic	+0.31, 0.34, 0.32, Av. +0.33

With these acids there does not seem to be any very important change in relative strength with salt concentration in this range.

Discussion

Specific variations in relative strengths of acids and bases with changing solvent have been rather generally interpreted in terms of a theory[14] according to which the change in relative strength should be a function of the charge and radius of the ion and of the dielectric constant of the medium. The dependence upon ionic charge has been verified qualitatively by Brönsted,[14c] and the predicted linear dependence upon the reciprocal of the dielectric constant has been shown by Wynne-Jones[14d] to be satisfactorily fulfilled by the existing conductivity data for the solvents water, and methyl and ethyl alcohols.[15] That the variations in relative strength of closely related carboxylic acids should depend upon changes in ionic size seems, however, not very probable and the present results support a different interpretation which re-

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(14) (a) Born, *Z. Physik*, **1**, 45 (1920); (b) Bjerrum and Larsson, *Z. physik. Chem.*, **127**, 358 (1927); (c) Brönsted, *Chem. Rev.*, **5**, 231 (1928); (d) Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

(15) The data obtained in this investigation do not agree with the relationship proposed by Wynne-Jones, but do not provide a fair test of it, since they were obtained in solutions of fairly high ionic strength. Both the theory and its previous tests apply to solutions of zero ionic strength. Our few colorimetric measurements at low ionic strengths do not indeed indicate large variations of relative strength with change in salt concentrations but are not sufficiently comprehensive to be conclusive.

cently has been discussed by Schwarzenbach and Egli.[16]

It should be noted first that there is a marked difference in behavior between acids in which the substituent is adjacent to the carboxyl group and those in which the substituent is more distantly located. Considering only the distantly substituted acids, it appears that any substitution which causes an increase in absolute strength causes an increase in relative strength, while one which causes a decrease in absolute strength causes a decrease in relative strength when the substituted and unsubstituted acids are transferred from water to *n*-butyl alcohol. This generalization is in accord with the expression which gives the additional electrical work ΔW required to ionize an acid containing a substituted polar group as compared with the unsubstituted acid in a solvent of dielectric constant D[16,17]

$$\Delta W = e\,\mu \cos \Theta/Dr^2$$

where r is the distance from the dipole to the carboxyl group, $\mu \cos \Theta$ is the component of the electric moment of the substituent along r, and e is the charge on the ion. A change in solvent resulting in a decrease in dielectric constant of the medium should therefore result in a change in relative strength, the direction of which should depend upon the influence of the substituent upon the ionization of the acid. For example, if the substitution results in an increase in ionization, ΔW is negative in sign and a change to a solvent of lower dielectric constant should result in an increase in relative strength; when substitution results in a decrease in ionization, ΔW is positive and a similar change in solvent should result in a decrease in relative strength. Thus meta and para nitro and chloro benzoic acids show an increase in strength relative to benzoic when transferred to *n*-butyl alcohol solution while meta- and para-methylbenzoic and para-methoxybenzoic acids show a decrease in strength. Similarly, beta-chloropropionic acid shows an increase in strength relative to propionic in agreement with the result expected from the fact that this acid is stronger than propionic acid in aqueous solution.

The changes in relative strength observed for ortho substituted benzoic acids and alpha substituted aliphatic acids show, however, that some quite different effect is involved when the substitution is near the carboxyl group. With the exception of *o*-hydroxy and *o*-methoxybenzoic acids, all of the ortho compounds studied decrease in strength relative to benzoic despite the fact that all substituents in this position cause an increase in the absolute strength of the acid. Likewise, chloroacetic and dichloroacetic acids decrease in strength relative to acetic. These results are similar to those obtained by Schwarzenbach[16] on the effects of substitution on the relative strengths of phenols and thiophenols in water and ethyl alcohol solutions. He concluded that while the results obtained on meta and para compounds could be explained fairly satisfactorily in terms of the electric moments of the substituents, other factors became predominant in the case of ortho substituted compounds.

It seems indeed to be a rather generally valid principle that the effects of an adjacent and of a distant substituent upon the reactions of a particular group in an organic molecule depend upon entirely different properties of the substituent. This is a familiar fact in the kinetics of reactions where an ortho substituent gives rise to a "steric hindrance."[18] With respect to equilibrium quantities it was noted by Flürscheim[19] that the introduction of any substituent into the ortho position in benzoic acid, regardless of its so-called electrochemical nature, has the effect of increasing the strength of the acid. Smallwood[17d] noted that all ortho substituted benzoic acids have especially large temperature coefficients of ionization.

Summary

1. A method for the measurement of the relatives strengths of acids in *n*-butyl alcohol has been developed.

2. The relative strengths of thirty-three representative carboxylic and phenolic acids have been measured.

3. The effect of a substituent upon the variation in relative strength with changing medium is that to be expected from the electric moment of the substituent and the dielectric constant of the medium when the substituent is introduced into the molecule at a point considerably removed from

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(16) Schwarzenbach and Egli, *Helv. Chim. Acta*, **17**, 1176, 1183 (1934).

(17) (a) Waters, *Phil. Mag.*, **8**, 436 (1929); (b) Wolf, *Z. physik. Chem.*, **B3**, 128 (1929); (c) Briegleb, *ibid.*, **B10**, 205 (1930); (d) Smallwood, THIS JOURNAL, **54**, 3048 (1932); (e) Eucken, *Z. angew. Chem.*, **45**, 203 (1932).

(18) See Hammett, *Chem. Rev.*, **17**, 125 (1935).

(19) Flürscheim, *J. Chem. Soc.*, **95**, 718 (1909). See also Lapworth and Manske, *ibid.*, 2533 (1928).

the carboxyl group. Some other influence is however preponderant when the substitution is adjacent to the carboxyl group, that is to say when it is on the alpha carbon in an aliphatic acid, or in the ortho position in benzoic acid.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Mechanism of the Slow Oxidation of Propane

BY ROBERT N. PEASE

In his original work[1] on the non-explosive oxidation of propane and the butanes, the writer was especially impressed with the fact that the oxidation reactions induced the dissociation of the hydrocarbons into the normal products, *e. g.*

$$C_3H_8 \longrightarrow C_3H_6 + H_2$$
$$\longrightarrow C_2H_4 + CH_4$$

This was discussed briefly in terms of what would now be called an "energy-chain." Since this work was done, F. O. Rice has brought out his "radical-chain" theory of hydrocarbon dissociation.[2] In view of the success of this theory in accounting for such experiments as those of Frey[3] on the dissociation of *n*-butane induced by decomposing dimethyl-mercury, it appeared important to attempt to account for the reactions occurring in hydrocarbon–oxygen mixtures in terms of radical-chains. For this purpose additional information about the products of the reactions was required.

In approaching this problem—the determination of liquid as well as gaseous reaction products—we were at first "side-tracked" by the discovery that substantial quantities of organic peroxides (other than per-acids) were formed.[4] However, it was eventually found that these peroxides could be largely eliminated (by coating the reaction tube with potassium chloride) without greatly affecting the reaction rate, an observation which convinced us that peroxides took no main part in the development of reaction. Had peroxides proven of greater importance, we would have been inclined toward Egerton's energy-chain theory.[5] An exhaustive search for other liquid oxidation products was then undertaken, the result of which was to show that, in the case of propane, only methanol and formaldehyde were of any importance. However, conditions were not favorable to the production of anything like stoichiometric yields of these, and the tentative conclusion was reached that the true primary products had still to be discovered.

Further investigation of this problem now indicates that methanol and formaldehyde, in addition to carbon monoxide and water, are in fact the primary products of propane oxidation, the indicated stoichiometric equation being

$$C_3H_8 + 2O_2 \longrightarrow CH_3OH + HCHO + CO + H_2O$$

How the general result is to be expressed in terms of the radical-chain theory will be discussed following presentation of the experimental data.

Experimental

The general methods of the previous investigations were employed. The gases passed at a known rate through a heated reaction tube of Pyrex glass coated with potassium chloride. Liquid products were separated at $-40°$, while gaseous products were separately collected over water with the trap at 0°. Methanol was determined by reaction with acetic anhydride (forty-eight hours at room temperature); formaldehyde by the potassium cyanide method; total aldehydes by the bisulfite method; esters by saponification following the alcohol determination. Carbon dioxide was absorbed in caustic; higher olefins (designated C_nH_{2n}) in concentrated sulfuric acid; ethylene in bromine water; oxygen in "Oxsorbent." Hydrogen and carbon monoxide were oxidized over copper oxide at 350°; paraffins were oxidized at 600°.

It was desirable to eliminate the olefin-producing reactions as far as possible. For this purpose, the experiments were conducted at low temperatures (300°, with one set at 260°). This necessitated the use of rather large reaction tubes. In order to minimize secondary oxidations, only mix-

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[1] Pease, THIS JOURNAL, **51**, 1839 (1929).

[2] F. O. and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935.

[3] Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

[4] Pease and Munro, THIS JOURNAL, **56**, 2034 (1934).

[5] Egerton, *Nature*, **121**, 10 (1928); "Activation et Structure des Molecules," Société de Chimie Physique, 1928, p. 489.