The Journal of the American Chemical Society

VOL. 54 SEPTEMBER, 1932 No. 9

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

RELATIONS BETWEEN THE STRUCTURE AND STRENGTH OF CERTAIN ORGANIC BASES IN AQUEOUS SOLUTION

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RECEIVED MARCH 23, 1932 PUBLISHED SEPTEMBER 5, 1932

Introduction

Surprise at the relatively great strength as a base of diethylaniline ($K_B = 3 \times 10^{-8}$) in relation to ethylaniline ($K_B = 1 \times 10^{-9}$)[1] and dimethylaniline ($K_B = 1 \times 10^{-9}$) was the starting point of this study. Bredig[2] had years ago shown that diethylamine is also exceptionally strong among its near homologs, although the differences are not so great as with the anilines. We measured the strength of thirty-eight amines of various types which had not previously been examined. For comparison, we also redetermined, under like conditions, the strength of twenty-two bases that had been previously studied. The new compounds were chosen as far as possible to throw light upon the effect of alkyl substituents in various combinations, but the effects of other groups were also considered.

Cells containing liquid junctions, in which a hydrogen electrode is surrounded by a buffer mixture of the base and its salt, are satisfactory for the purpose in hand, although the results are not as unambiguous as those obtained in cells without transference. The chief difficulties in this method arise when the base studied is very weak, very strong or very insoluble in water. Many of the bases which we examined had very low solubilities in water at 25°, and for these a special extrapolation method had to be used. Michaelis and Mizutani[3] have shown that when the apparent strength of a base (or acid) in logarithmic units is plotted against the alcohol content of the solution for decreasing percentages of alcohol, the form of the curve obtained is always such as to permit a satisfactory extrapolation to the

[1] (a) Pring, *Trans. Faraday Soc.*, **19**, 705–17 (1924); (b) see Hall, THIS JOURNAL, **52**, 5125 (1930).

[2] Bredig, *Z. physik. Chem.*, **13**, 191 (1894).

[3] Michaelis and Mizutani, *ibid.*, **116**, 135–159 (1925); **118**, 318–326, 327–341 (1925).

strength value for pure water. We followed their method in many cases as shown by Fig. 1.

In the course of the work it became desirable to know the effect of temperature on the strength of many of the bases and this was determined in several cases over the range from 19 to 32°.

Experimental

Our cells were mostly of the type

$$\mathrm{Pt} \left| \mathrm{H_2} \right| \begin{matrix} \text{Base, } C = C_B, \\ \text{Salt, } C = C_{BH^+} \end{matrix} \left| \begin{matrix} \text{KCl,} \\ \text{Satd.} \end{matrix} \right| \begin{matrix} \text{KCl, satd.} \\ \mathrm{Hg_2Cl_2}\text{, satd.} \end{matrix} \left| \mathrm{Hg} \right.$$

They were not thermostated, but the temperatures were measured in different parts of the cells and corrections made as described below. The apparatus presented few novel features and its detailed description is omitted.

Most of the bases were purchased from the Eastman Kodak Company—a few from other manufacturers. Several were prepared in the Organic Chemical Laboratory of this University and kindly presented to us.

Liquid bases were redistilled in a carbon dioxide-free atmosphere and characterized by their boiling points. Solid bases were considered of sufficient purity if they gave correct melting points; otherwise they were recrystallized until a constant and correct melting point was reached.

Other materials were of ordinary C. P. grade further purified when necessary.

Notation.—We define an experimental quantity paH in terms of equation 1.

$$paH = \frac{E - E_{cal.}}{0.00001983(273.1 + t)} \qquad (1)$$

where E is the e. m. f. of a cell of the type described, $E_{cal.}$ is taken as $0.2448 - 0.008(t - 25°)$ and t is the centigrade temperature of the calomel electrode.

Letting

$$paH = pcH + pfH \qquad (2)$$

where cH is the stoichiometric concentration of free strong acid in the cell, pfH may be determined with varying concentrations of strong acids and salts in the cells. This has been done by Bjerrum and Unmack,[4] who give cube root interpolation formulas for pfH over a large range of concentrations of sodium chloride and potassium chloride. We made two series of measurements of this type, one in solutions of pure hydrochloric acid and one in mixtures of hydrochloric acid and guanidine chloride. Our results at low concentrations agreed well with Bjerrum and Unmack's but at higher concentrations many individual ion effects were noticeable.

[4] Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.*, IX, 1 (1929).

Every new substance measured constitutes a special case, and it is in principle impossible to be sure that an adopted *pfH* value is the correct one for a given mixture of any particular base and salt. Nevertheless, in rather dilute and nearly neutral solutions there is a very strong presumption that no serious error will be introduced by adopting any of the values of *pfH* given by different authors, while in concentrated, strongly acid or strongly alkaline solutions, unavoidable uncertainties will be introduced by the use of any set of values for *pfH*. In view of these considerations, and in the hope of making our values as self-consistent and comparable among themselves as possible, we decided to use in all cases *pfH* values calculated from the cube-root interpolation formulas of Bjerrum and Unmack. The value 0.2448 for the saturated calomel electrode was used in order to make our practice consistent with that of the Danish investigators as far as possible. Had the value recommended by Clark been used, our values of $pK_{H(c)}$ would have been 0.02 or 0.03 units lower in most cases.

We now define a constant $K_{H(c)} = C_B \times C_{H_3O^+}/C_{BH^+} = K_{H(o)} \times f_{BH^+}/f_{H_3O^+} \times 1/fB$ where $K_{H(o)}$ is the thermodynamic mass action constant $a_B \times a_{H^+}/a_{BH^+}$ for the dissociation in water of the cation acid BH^+. Because of the form of the activity coefficient terms involved $K_{H(c)}$ may be expected to be very nearly independent of salt concentration in dilute solution—much more nearly so than the "constant" K_B usually given to characterize the strength of a base. Moreover, $pK_{H(c)}$ is more directly obtainable from the measurements and involves no assumption concerning the value of K_w. In fact

$$pK_{H(c)} = pcH + pR \qquad (3)$$

where R is the ratio of the stoichiometric concentrations of free base and salt, and *pcH* is obtained from *paH* by (2).

The Effect of Hydrolysis.—If a 1:1 base–salt mixture is found to be acid or alkaline the acid or alkali has been produced at the expense of the salt or base according to (a) or (b).

$$\begin{aligned} &(a) \quad BH^+ + H_2O \rightleftharpoons B + H_3O^+ \\ &(b) \quad B + H_2O \rightleftharpoons BH^+ + OH^- \end{aligned} \qquad (4)$$

It is therefore necessary to calculate *cH* and *cOH* from *paH* and to apply appropriate corrections to the concentrations of base and salt originally introduced.[5] At an ionic strength of 0.01 this correction to *pR* amounts to less than 0.01 between $paH = 4.2$ and $paH = 9.8$ inclusive, but becomes appreciable when the base is very strong or very weak, as well as in more dilute solutions.

Results

For convenience in discussion the bases are divided into several groups. Group I includes rather weak bases (pK_H between 3 and 7), which were

[5] These corrections are illustrated below.

TABLE I

1 No.	2 Name	3 *paH*	4 *t*	5 *c*	6 *pcH*	7 *pR*	8 $pKH_{(t)}$	9	10 $pKH_{(25°)}$	11
1	β-Acetylpyridine	3.26	25	0.0100	3.23	−0.05	3.18	0.011	3.18	
2	N-Methyl-α-naphthylamine	3.82	27	.0010	3.81	− .14	3.67	.013	3.70	
3	α-Naphthylamine	4.10	22	.0005	4.09	− .13	3.96	.013	3.92	3.92[b]
4	β-Naphthylamine	4.25	23	.0005	4.24	− .10	4.14	.013	4.11	4.25[c]
5	*m*-Phenetidine	4.16	28	.0100	4.13	.00	4.13	.013	4.17	
6	*m*-Anisidine	4.27	22	.0100	4.24	.00	4.24	.013	4.20	
7	*o*-Toluidine	4.42	25	.0100	4.39	.00	4.39	.014	4.39	4.43[a]
8	*o*-Phenetidine	4.46	28	.0100	4.43	.00	4.43	.014	4.47	
9	*o*-Anisidine	4.59	20	.0100	4.56	.00	4.56	.014	4.49	
10	Aniline	4.67	21	.0100	4.64	.00	4.64	.014	4.58	4.62[d]
11	N-Methyl-*o*-toluidine	4.65	23	.0100	4.62	.00	4.62	.014	4.59	
12	*m*-Toluidine	4.72	25	.0100	4.69	.00	4.69	.014	4.69	4.71[a]
13	N-Ethyl-*o*-toluidine	4.99	22.5	.0040	4.96	.00	4.96	.015	4.92	
14	N-Methyl-*m*-toluidine	5.03	21	.0100	5.00	.00	5.00	.015	4.94	
15	α-Hydroxy-β-ethylpyridine	5.03	25	.0100	5.00	.00	5.00	.015	5.00	
16	N-Dimethylaniline	5.08	25.5	.0040	5.05	.00	5.05	.015	5.06	5.10[a]
17	*p*-Toluidine	5.11	24	.0100	5.08	.00	5.08	.015	5.07	5.12[a]
18	*p*-Phenetidine	5.23	28	.0100	5.20	.00	5.20	.015	5.25	
19	*p*-Anisidine	5.36	22.5	.0100	5.33	.00	5.33	.015	5.29	
20	N-Methyl-*p* toluidine	5.39	23	.0100	5.36	.00	5.36	.015	5.33	
21	N-Dimethyl-*p*-toluidine	5.58	21.5	.00125	5.56	.00	5.56	.016	5.50	5.55[e]
22	N-Ethyl-*p*-toluidine	5.75	22	.0050	5.72	.00	5.72	.016	5.67	
23	N-Dimethyl-*o*-toluidine	5.90	20	.0025	5.94	.00	5.94	.016	5.86	5.96[e]

[a] *Cf.* Hall, THIS JOURNAL, **52**, 5115 (1930). [b] Farmer and Warth (F. W.), *J. Chem. Soc.*, **85**, 1713 (1904). [c] 4.23 F. W., 4.27 McCoy, private communication. [d] Average from literature. [e] Ley and Grau, *Ber.*, **58B**, 1765–1775 (1925).

sufficiently soluble to be studied in water solution. Results for these are collected in Table I. The columns of the table present in order: (1) a serial number to aid in identifying the base, (2) its name, (3) the value of *paH* as measured, (4) the centigrade temperature, (5) the concentration of the base (and of the salt) added, (6) the value of *pcH* obtained by subtracting from *paH* the appropriate value of *pfH* calculated from Bjerrum and Unmack's formulas, (7) *pR* (R = log (cB/cBH$^+$), (8) the negative logarithm of the hydrolysis constant calculated for the temperature of the measurement, (9) the negative temperature coefficient of the constant, and (10) the constant corrected to 25°. In column (11) are added for comparison some of the "best" values obtainable from the literature.

Group II contains the stronger bases (pK_H between 7 and 12) of the same solubility class, results for which appear in Table II. In this table the first six and the last five columns are the same as in Table I. Column (7) shows $pK_{w(c)}$ for the appropriate concentration and temperature (from Bjerrum and Unmack) and column (8) $pcOH = pK_{w(c)} - pcH$.

(A sample calculation (for No. 28, 1-ethylpiperidine) is as follows: *paH* at 23° of a mixture made up 0.01 N in free base and 0.01 N in salt was 10.45. At this concentration of electrolyte we find from Bjerrum and Unmack's tables $pfH = 0.03$, so that *pcH* is 10.42. $pK_{w(c)}$ for this concentration and temperature is 13.97, so that *pcOH* = 3.55. This means an hydroxyl-ion concentration of 0.00029, so that the ratio $R = (0.01 - 0.00029)/(0.01 + 0.00029)$ and $pR = 0.03$. The constant $pK_{H(c)}$ at 23° is then 10.42 + 0.03 or 10.45, and for a base of this strength the temperature coefficient of

TABLE II

1 No.	2 Name	3 paH	4 t	5 c	6 pcH	7 $pK_{w(c)}$	8 $pcOH$	9 pR	10 $pKH_{(t)}$	11 $-\alpha$	12 $pKH(25°)$	13
24	Triethanolamine	7.85	22	0.0100	7.82	14.00	6.18	0.00	7.82	0.018	7.77	
25	Diethanolamine	8.95	23	.0100	8.92	13.97	5.05	.00	8.92	.020	8.88	
26	2-Hydroxy-3-ethylpiperidine	9.12	25	.0050	9.09	13.92	4.83	.00	9.09	.020	9.09	
27	Ethanolamine	9.53	22	.0100	9.50	14.00	4.50	.00	9.50	.020	9.44	
28	1-Ethylpiperidine	10.45	23	.0100	10.42	13.97	3.55	.03	10.45	.021	10.41	
29	1-N-butylpiperidine	10.47	23	.0100	10.44	13.97	3.53	.03	10.47	.021	10.48	
30	N-Methyl-γ-phenyl-*n*-propylamine	10.63	22.5	.0100	10.60	13.99	3.39	.04	10.64	.022	10.58	
31	*n*-Butylamine	10.71	20	.0100	10.68	14.07	3.39	.04	10.72	.022	10.61	
32	Cyclohexylamine	10.65	24	.0100	10.62	13.93	3.31	.04	10.66	.022	10.64	
33	*n*-Amylamine	10.70	22	.0100	10.67	14.00	3.33	.04	10.71	.022	10.64	
34	Isoamylamine	10.70	22	.0100	10.67	14.00	3.33	.04	10.71	.022	10.64	10.60[a]
35	1-Ethyl-2-methylpiperidine	10.64	26	.0100	10.69	13.87	3.26	.05	10.66	.022	10.68	
36	1-*n*-Butyl-2-methylpiperidine	10.54	26	.0020	10.52	13.91	3.39	.18	10.70	.022	10.72	
37	N-Methyl-δ-phenyl-*n*-butylamine	10.78	23	.0100	10.75	13.97	3.22	.05	10.80	.022	10.76	
38	Di-isobutylamine	10.88	21	.0100	10.85	14.04	3.19	.06	10.91	.022	10.82	10.59[a]
39	2-Methylpiperidine	10.97	23.2	.0100	10.94	13.96	3.02	.08	11.02	.022	10.98	
40	Diethylamine	10.92	25	.0100	13.90	13.90	3.01	.09	10.98	.022	10.98	11.00[a]
41	Di-isopropylamine	11.07	21	.0100	11.04	14.04	3.00	.09	11.13	.022	11.05	
42	Di-*n*-butylamine	11.28	21	.0100	11.25	14.04	2.79	.14	11.39	.022	11.31	

[a] Bredig, Ref. 2, as corrected in "International Critical Tables."

TABLE III

1 No.	Name	3 *paH*	4 *t*	5 *c*	6 *pcH*	7 $pK_{w(o)}$	8 *pcOH*	9 *pR*	10 $pKH_{(t)}$	11 $-\alpha$	12 $pKH_{(25°)}$	13
43	2-Aminodiphenyl	3.93	22	0.0010	3.92	...	..	−0.10	3.82	0.013	3.78	
44	N-Ethyl-α-naphthylamine	4.28	29	.0010	4.24	...	..	− .05	4.19	.013	4.24	
45	4-Aminodiphenyl	4.28	29	.0010	4.27	...	..	− .05	4.22	.013	4.27	
46	N-Methylaniline	4.85	27	.0100	4.82	...	..	.00	4.82	.015	4.85	4.75[a]
47	N-Dimethyl-α-naphthylamine	4.86	28	.0005	4.85	...	..	.02	4.83	.015	4.88	
48	N-*n*-Propylaniline	5.06	24	.0020	5.04	...	..	.00	5.04	.015	5.02	
49	N-Ethylaniline	5.15	24	.0020	5.15	...	..	.00	5.62	.016	5.11	5.15[a]
50	N-Di-*n*-propylaniline	5.63	23	.0005	5.62	...	..	.00	5.68	.016	5.59	
51	N-Methyl-*n*-propylaniline	5.68	23	.0009	5.67	...	..	.00	5.67	.017	5.64	
52	N-Methylethylaniline	6.04	22	.0020	6.02	...	..	.00	6.02	.016	5.98	
53	N-Ethyl-*n*-propylaniline	6.40	22	.0008	6.39	...	..	.00	6.39	.016	6.34	
54	N-Diethylaniline	6.62	22	.0010	6.61	...	..	.00	6.61	.017	6.56	6.52[a]
55	N-Diethyl-*p*-toluidine	7.14	23	.0005	7.13	14.03	6.90	.00	7.13	.018	7.09	
56	N-Diethyl-*o*-toluidine	7.25	21	.0005	7.24	14.10	4.09	.00	7.24	.018	7.18	
57	Tri-*n*-butylamine	9.87	25	.0010	9.86	13.95	4.09	+ .07	9.93	.021	9.93	
58	s-Diphenylguanidine	10.02	25	.0010	10.01	13.95	3.94	+ .11	10.12	.021	10.12	10.0[a]
59	Di-isoamylamine	10.78	27.8	.0040	10.75	13.82	3.07	+ .19	10.94	.022	11.00	10.89[a]
60	Di-*n*-amylamine	10.82	26	.0020	10.80	13.91	3.11	+ .36	11.16	.022	11.18	

[a] *Cf.* Hall, Ref. 1.

$pKH(c)$ is -0.021. We must therefore subtract 0.04 from the value at 23° to give 10.41 as the final value of the constant at 25°.

All the constants given in Tables I, II and III were calculated similarly.)

Group III, reported in Table III, includes the bases studied in alcoholic solution (either because they were very insoluble in water, or for comparison purposes). The meanings of the various columns in the table correspond to those in Tables I and II. The concentrations were so low in the case of these bases that the corrections for *pfH* are very small. Figure 1 shows the method of obtaining the value of *paH* by extrapolation from solutions progressively less alcoholic. In this figure abscissas represent increasing percentage of alcohol, and ordinates the observed e. m. f. of the cells containing the base–salt mixtures.

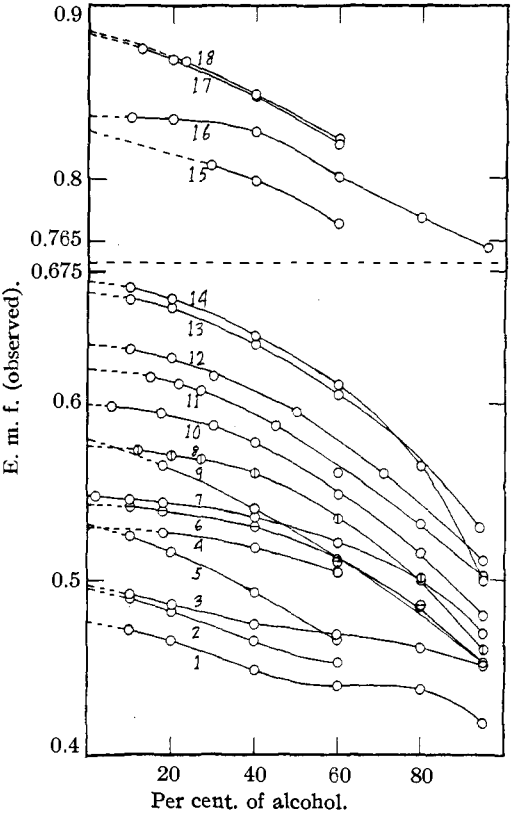

Fig. 1.—Effect of alcohol on apparent strength of bases: ordinates, observed voltages of cells; abscissas, percentage of ethanol by volume. Numbers of curves: 1, 2-aminodiphenyl; 2, ethyl-α-naphthylamine; 3, 4-aminodiphenyl; 4, methylaniline; 5, dimethyl-α-naphthylamine; 6, *n*-propylaniline; 7, ethylaniline; 8, di-*n*-propylamine; 9, methyl-*n*-propylaniline; 10, methylethylaniline; 11, ethyl-*n*-propylaniline; 12, diethylaniline; 13, diethyl-*p*-toluidine; 14, diethyl-*o*-toluidine; 15, tri-*n*-butylamine; 16, diphenylguanidine; 17, di-isoamylamine; 18, di-*n*-amylamine.

Guanidine.—As this proved to be a quite exceptionally strong base, a special method was used to determine its strength.

To 20 cc. of 2 *N* potassium chloride was slowly added an equal volume of 2 *N* potassium hydroxide. The *paH* was determined after each addition of potassium hydroxide. The results are reported in Table IV.

The third line of Table IV is the sum of the first two and is the value of $pK_{w(inc.)} = paH + pcOH$. The exact constancy of this value is surprising even in view of the fact that the ionic strength was maintained constant throughout the experiment. (The value found by Bjerrum and Unmack

TABLE IV

$pK_{w(inc.)}$ IN POTASSIUM HYDROXIDE SOLUTION

pcOH	2.00	1.28	0.97	0.81	0.72	0.57
paH	11.94	12.65	12.96	13.12	13.21	13.36
$pK_{w(inc.)}$	13.94	13.93	13.93	13.93	13.93	13.93
pcOH	0.47	0.34	0.11	0.07	0.03	0.00
paH	13.46	13.59	13.82	13.87	13.90	13.93
$pK_{w(inc.)}$	13.93	13.93	13.93	13.94	13.93	13.93

in 1.5 *N* potassium chloride is 13.91.) A similar experiment was now carried out, using guanidine chloride instead of potassium chloride. From the values of *paH* found corresponding values of *pcOH* were calculated (using 13.91 instead of 13.93 as the value of $pK_{w(inc.)}$, as this series of measurements was made at 24.2° instead of at 23.5°). From these values of *pcOH* (found) and the known amounts of potassium hydroxide added, it was possible to calculate very simply the concentration of free base and of salt. From these data may be calculated a constant

$$pK_{H(inc.)} = pK_{H(c)} + pfH = paH + pR$$

The values of this constant are reported in Table V.

TABLE V

STRENGTH CONSTANT OF GUANIDINE

(*x* = concn. of potassium hydroxide introduced)

x	0.1422	0.1966	0.2817	0.4305	0.5454
paH	12.37	12.53	12.73	12.97	13.13
cOH found	0.0288	0.0417	0.0660	0.1147	0.1660
R	0.065	0.094	0.145	0.252	0.352
$pK_{H(inc.)}$	13.56	13.56	13.57	13.57	13.58
x	0.6760	0.7895	0.8880	0.9441	1.000
paH	13.27	13.42	13.50	13.56	13.60
cOH found	0.2290	0.3235	0.3890	0.4465	0.5246
R	0.507	0.625	0.828	0.896	0.905
$pK_{H(inc.)}$	13.56	13.62	13.58	13.64	13.64
				Mean =	13.59

To calculate $pK_{H(c)}$ from this constant it would be necessary to know the value of *pfH*. This cannot be calculated from our data. Bjerrum and Unmack's formula is not supposed to be valid above 1.5 normal, or in as strongly alkaline solutions as ours. On the very doubtful assumption that their formula is valid in solutions 2 *N* in electrolyte and up to 1 *N* in potassium hydroxide, we find $pfH = -0.09$, from which we calculate for guanidine $pK_{H(c)} = 13.68$ at 24.2°. We have no information on the temperature coefficient for such a strong base, but we may perhaps assume as the most probable value of the constant at 25° $pK_{H(c)} = 13.6_5$.

The Temperature Coefficient of pK_H.—The information in the literature regarding the effect of temperature on the dissociation of bases is

meager. As we needed some rational means of reducing our own results and those of others to a single standard temperature, we measured the constants of several bases at temperatures ranging from 19 to 32°. Three significant conclusions may be drawn from the results: (1) in all cases the value of pK_H diminished with rising temperature, (2) the change with temperature increased with the value of pK_H, (3) where sufficient data were obtained to test the question, the change of pK_H with temperature appears to be linear. The value of pK_H was calculated at each temperature as indicated in the tables. The results are reproduced in Fig. 2, where, however, through error the lower point of curve 8 has been placed 0.01 unit too low. The results are assembled in Table VI.

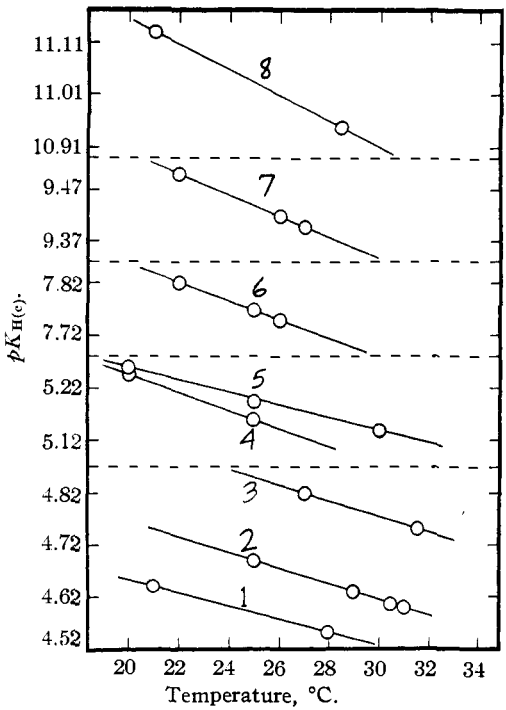

Fig. 2.—Temperature coefficient of $pK_{H(c)}$: ordinates, $pK_{H(c)}$; abscissas, temperature in °C. Numbers of curves: 1, aniline; 2, *m*-toluidine; 3, methylaniline; 4, dimethylaniline; 5, pyridine; 6, triethanolamine; 7, ethanolamine; 8, di-isopropylamine.

The values of the temperature coefficient were plotted against $pK_{H(25°)}$ and a straight line was drawn through the points. From this graph were read the values of $-\alpha$ used in Table I (column 9) and Tables II and III (column 11).

TABLE VI

Base	*t*, °C.	pK_H	$\Delta pK_H/\Delta t$	No. of curves in Fig. 2
Aniline	21.0	4.65		
	28.0	4.55	−0.0129	1
m-Toluidine	25.0	4.69		
	29.0	4.63		
	30.5	4.61		
	31.0	4.60	− .0150	2
Methylaniline	27.0	4.82		
	31.5	4.75	− .0156	3
Dimethylaniline	20.0	5.25		
	25.0	5.16	− .0180	4[a]

TABLE VI (*Concluded*)

Base	t, °C.	pK_H	$\Delta pK_H/\Delta t$	No. of curves in Fig. 2
Pyridine	20.0	5.26		
	25.0	5.19		
	30.0	5.14	−0.0120	5[b]
Triethanolamine	22.0	7.82		
	25.0	7.77		
	26.0	7.75	− .0175	6
Ethanolamine	22.0	9.50		
	26.0	9.42		
	27.0	9.40	− .0200	7
Di-isopropylamine	21.0	11.13		
	28.5	10.96	− .0227	8

[a] Goldschmidt and Keller, *Ber.*, **35**, 3534–3549 (1902). [b] Hahn and Klockman, *Z. physik. Chem.*, **146**, 373–403 (1930).

Discussion of Results

Positive Groups.—Bredig[2] showed that the introduction of one alkyl group into ammonia increased the pK_H by approximately 1.3, while a second alkyl group had a much smaller effect (*ca.* 0.4 of a pK_H unit) and that except in the case of the methyl amines, the tertiary compound was of about the same strength as the primary. We have made only a few additions to the values already known for this class of compounds, and our results confirm the earlier data for the most part. Table VII gives the data at present available, and shows that the behavior of the methylamines referred to above is paralleled by the *n*-butylamines.

TABLE VII

NH_3 pK_H = 9.27

R	$\Delta pK_H(1)$	RNH_2	$\Delta pK_H(2)$	R_2NH	$\Delta pK_H(3)$	R_3N
CH_3	1.37	10.64	0.07	10.71	−0.91	9.80
					$(CH_3(C_2H_5)_2)$	10.34
C_2H_5	1.40	10.67	.31	10.98	−0.24	10.74
n-C_3H_7	1.31	10.58	.33	10.91	− .26	10.65
iso-C_3H_7	1.36	10.63	.42	11.05*	....	...
n-C_4H_9	1.34	10.61*	.70	11.31*	−1.38	9.93*
iso-C_4H_9	1.15	10.42	.40	10.82	−0.50	10.32
sec.-C_4H_9	1.29	10.56	...	...	....	...
tert.-C_4H_9	1.18	10.45	...	...	....	...
n-C_5H_{11}	1.37	10.64*	.54	11.18*	....	...
iso-C_5H_{11}	1.37	10.64	.36	11.00	....	...
cyclo-C_6H_{13}	1.37	10.64*	...	...	....	...
Average	1.32		.39		−0.66	

In Table VII the values marked * refer to compounds which we believe we have measured for the first time. For the other figures we have used our

own results where available, or made the best selection we could from the values in the literature.[6]

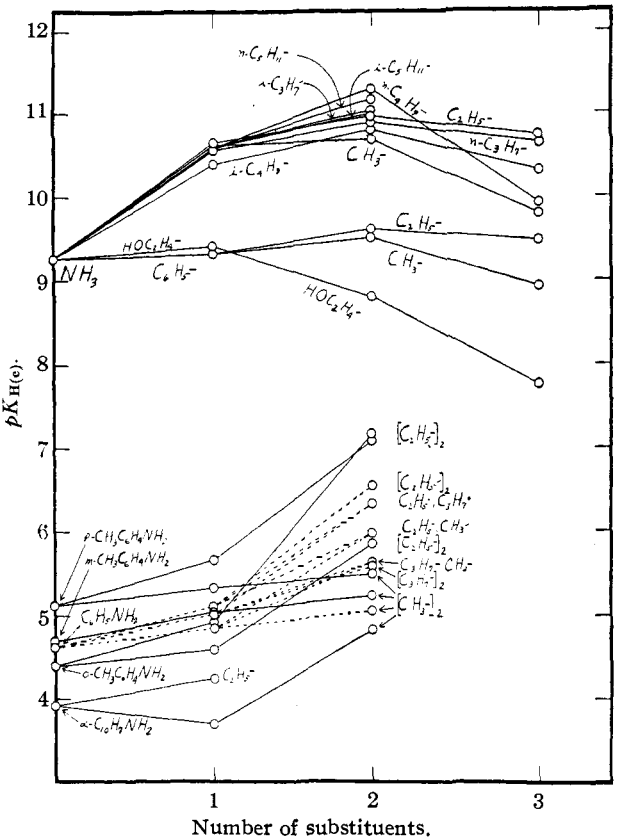

Fig. 3.—Effect of alkyl groups on strength of aliphatic and aromatic amines: ordinates, $pK_{H(c)}$; abscissas, number of substituent groups.

The data are also reproduced in Fig. 3, which clearly shows the high relative base strength of the secondary amines. Very similar relations are observed among the N-alkyl benzylamines, as Table VIII shows.

TABLE VIII

STRENGTH OF BENZYLAMINES

	pK_H		pK_H		pK_H
$C_6H_5CH_2NH_2$	9.34[a,b]	$C_6H_5CH_2NHCH_3$	9.58[b]	$C_6H_5CH_2N(CH_3)_2$	8.93[a]
		$C_6H_5CH_2NHC_2H_5$	9.68[b]	$C_6H_5CH_2N(C_2H_5)_2$	9.48[a]

Average $\Delta pK_H = +0.29$.

[a] "International Critical Tables," Vol. VI. [b] Carothers, Bickford and Hurwitz, THIS JOURNAL, 49, 2908 (1927).

[6] *Cf.* Hall, THIS JOURNAL, 52, 5115–5128 (1930).

Although the replacement of one H in CH_3 by C_6H_5 makes the benzylamine as weak as ammonia, the substitution of methyl and ethyl for the other hydrogen atoms first increases the strength and then markedly decreases it in the tertiary amines. Inspection of the last two tables shows that a single alkyl group has almost exactly the same effect on the strength, whatever its nature. The effect of the second alkyl group increases with length and degree of branching of the chain as far as the normal butyl radical, and then falls off again. A third alkyl group weakens the secondary amine in all cases, but especially in the methyl and *n*-butyl compounds.

Effect of Methyl.—The following Table IX shows the very constant positive effect of the methyl group as a second substituent on the nitrogen atom, and also the decreasing effect of an additional CH_2 group as the hydrocarbon chain is lengthened.

TABLE IX

	pK_H	ΔpK_H		pK_H
Aniline	4.62	+0.23	N-Methylaniline	4.85
ΔpK_H = +4.72			ΔpK_H = +4.73	
Benzylamine	9.34*	+ .24	N-Methylbenzylamine	9.58*
ΔpK_H = +0.49			ΔpK_H = +0.56	
β-Phenylethylamine	9.83*	+ .31	N-Methyl-β-phenylethylamine	10.14*
ΔpK_H = +0.37			ΔpK_H = +0.44	
γ-Phenyl-*n*-propylamine	10.20*	+ .38	N-Methyl-γ-phenyl-*n*-propylamine	10.58
ΔpK_H = +0.20			ΔpK_H = +0.17	
δ-Phenyl-*n*-butylamine	10.40*	+ .35	N-Methyl-δ-phenyl-*n*-butylamine	10.75
ΔpK_H = +0.09				
ε-Phenyl-*n*-amylamine	10.49*			

The starred values are from Carothers' paper,[7] while aniline and methylaniline are average values from the literature. The last two values in the right-hand column are from our own data. Similar effects of the methyl group appear below in the discussion of the piperidines, anilines, toluidines, etc.

Alkyl Piperidines.—Our measurements on this class of compounds show clearly two effects, portrayed in Table X. (1) The introduction of a methyl group in the 2-position increases the base strength by 0.3 unit except in the case of piperidine itself. (2) The introduction of an alkyl group on the nitrogen of the secondary amine has a weakening effect of about 0.7 unit quite comparable to the introduction of a third alkyl group into dimethyl- or diethylamine. The weakness of methylpiperidine in rela-

TABLE X

	pK_H		pK_H
Piperidine	11.13	2-Methylpiperidine	10.98
1-Ethylpiperidine	10.40	1-Ethyl-2-methylpiperidine	10.68
1-*n*-Butylpiperidine	10.42	1-*n*-Butyl-2-methylpiperidine	10.72

[7] Carothers, Table VIII, Ref. *b*.

tion to piperidine is surprising, and is comparable to the case of N-methyl-α-naphthylamine.

N-Alkylanilines, N-Alkyltoluidines and N-Alkyl-α-naphthylamines.—Although substitution of one alkyl group for one of the hydrogens attached to the nitrogen atom in these compounds usually (with the exception of methyl-α-naphthylamine) causes a moderate increase in the base strength as is to be expected, the surprising thing is the extent of the increase caused by the *second* alkyl substitution, particularly when the substituents are ethyl groups. This is the effect referred to in the introduction as the starting point of the investigation. As shown by Table XI and Fig. 3, the positive effect seems to reach a decided maximum with the ethyl group, although unfortunately measurements have not been made on the butyl or amyl derivatives.

TABLE XI

ANILINE $pK_H = 4.62$

	pK_H		pK_H
N-Methylaniline	4.85	N-Diethylaniline	6.56
N-Ethylaniline	5.11	N-Methyl-*n*-propylaniline	5.64
N-*n*-Propylaniline	5.02	N-Ethyl-*n*-propylaniline	6.34
N-Dimethylaniline	5.06	N-Di-*n*-propylaniline	5.59
N-Methylethylaniline	5.98		

The toluidines show many similarities to the anilines as will be seen from Table XII.

TABLE XII

	pK_H		pK_H		pK_H
o-Toluidine	4.39	N-Methyl-*o*-toluidine	4.59	N-Dimethyl-*o*-toluidine	5.86
m-Toluidine	4.69	N-Methyl-*m*-toluidine	4.94	N-Dimethyl-*m*-toluidine	5.24
p-Toluidine	5.12	N-Methyl-*p*-toluidine	5.33	N-Dimethyl-*p*-toluidine	5.50
		N-Ethyl-*o*-toluidine	4.92	N-Diethyl-*o*-toluidine	7.18
		N-Ethyl-*m*-toluidine	..	N-Diethyl-*m*-toluidine	..
		N-Ethyl-*p*-toluidine	5.67	N-Diethyl-*p*-toluidine	7.09

In every case we see a moderate increase in base strength due to the first N-methyl, a greater increase due to ethyl, or two methyl groups, and a very marked increase indeed for two ethyl groups. This effect is especially great in the ortho isomer. Dimethyl-*o*-toluidine is, surprisingly enough, stronger than dimethyl-*p*-toluidine. The average increase in strength due to a single methyl group is 0.2 unit, which is to be compared to the value 0.23 given above for methylaniline. An ethyl group produces an increase of about 0.5 unit. The data are included in Fig. 3.

The following few data are available on the derivatives of α-naphthylamine.

TABLE XIII

	pK_H		pK_H
α-Naphthylamine	3.92	N-Ethyl-α-naphthylamine	4.24
N-Methyl-α-naphthylamine	3.70	N-Dimethyl-α-naphthylamine	4.88

Here the methyl group produces an anomalous *decrease* in the strength, while two methyl groups produce a surprisingly large *increase*.

Anisidines and Phenetidines.—A single methoxy or ethoxy group decreases the strength of aniline when it is ortho or meta to the amino group, and increases it in the para position, as the following table shows. It is noteworthy that for both types of bases $\Delta pK_H(o-m)/\Delta pK_H(p-o) = {}^3/_8$, very nearly.

TABLE XIV

	Anisidines	pK_H		Phenetidines	pK_H
p-		5.29	*p*-		5.25
	$-\Delta pK_H = 0.80$			$-\Delta pK_H = 0.78$	
o-		4.49	*o*-		4.47
	$-\Delta pK_H = 0.29$			$-\Delta pK_H = 0.30$	
m-		4.20	*m*-		4.17

Effect of Saturation on the Aromatic Nucleus.—As is well known, piperidine is a much stronger base than pyridine. We have also found that cyclohexylamine is much stronger than aniline, as would be expected.

TABLE XV

Aniline	4.62	Pyridine	5.21
Cyclohexylamine	10.61	Piperidine	11.13
pK_H =	5.99		5.92

Ethanolamines.—The ethanol group appears to be intermediate in character between the positive alkyl groups and the much more strongly negative groups such as phenyl. Thus the first ethanol group makes ammonia slightly stronger, but the second and third have the opposite effect (see Fig. 3).

TABLE XVI

	pK_H		pK_H
Ammonia	9.27	Diethanolamine	8.88
Ethanolamine	9.44	Triethanolamine	7.77

Negative Groups

Effect of Phenyl.—The strongly negative influence of this group is well known, and may be recognized in the following data. (*Cf.* also Fig. 4.)

TABLE XVII

	pK_H		pK_H
Ammonia	9.27	Diphenylamine	0.85
Aniline	4.62	Triphenylamine	<0.0[a]

[a] Estimated from unpublished work on acetic acid solutions.

We have also secured evidence of its effect on the strength of guanidine, as will appear from Table XVIII.

TABLE XVIII

	pK_H		pK_H
Guanidine	13.65	Diphenylguanidine	10.12[b]
Phenylguanidine	10.77[a]	Triphenylguanidine	9.10

[a] Davis and Elderfield, THIS JOURNAL, **54**, 1499 (1932). [b] We calculate the value 10.01 at 18° from the work of Walden and Ulich, *Z. Electrochem.*, **34**, 25 (1928).

Other Negative Groups.—The negative effect of the nitro group appears to be especially strong on guanidine since α-nitroguanidine appears to have a constant in the neighborhood of zero, while guanidine itself has a value above thirteen.

The effect of chlorine, bromine, etc., is well known. It is not always realized, however, how entirely similar are the effects of these groups on acids and on bases (or more properly, on uncharged and cation acids). This is brought out in Figs. 4 and 5. Here we have shown the effect of phenol on guanidine, succinic acid and ammonia, and of chlorine on phenol, acetic acid and aniline. The data on the chlorophenols are from Tiessens'[8] paper except that the values of Hantzsch and of Mizutani[9] are used for *p*-chlorophenol instead of the very old and improbable value given by Bader.[10] The latter's value for *o*-chlorophenol is not included. The values for the chloroacetic and phenylsuccinic acids are taken from Landolt and Börnstein's Tables. The values given by Hall for the chloroanilines are used.

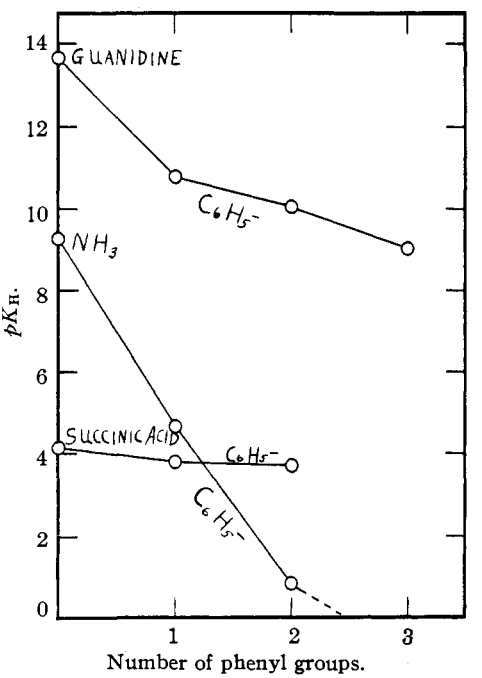

Fig. 4.—Effect of phenyl group on strength of guanidine, ammonia and succinic acid: ordinates, pK_H; abscissas, no. of phenyl groups.

The new facts reported in this paper seem to introduce no radically new principles into the doctrine of the effect of substituents on acid strength, although the great relative strength of *diethyl* compounds is perhaps of special significance, and the existing data have been supplemented at many points. Data of this type should be interpreted with caution for two reasons. In the first place

[8] Tiessens, *Rec. trav. chim.*, **48**, 1068 (1929).

[9] Landolt-Börnstein, "Tabellen."

[10] Bader, *Z. physik. Chem.*, **6**, 295 (1890).

the quantum theoretical basis for the reactions involved is still so obscure as to render discussions of "relative electron sharing ability" and the like of small significance, and in the second place any conclusions based on small variations of the constants (less than one logarithmic unit) are likely to have significance relative to a single solvent or class of solvents only.[1b,11]

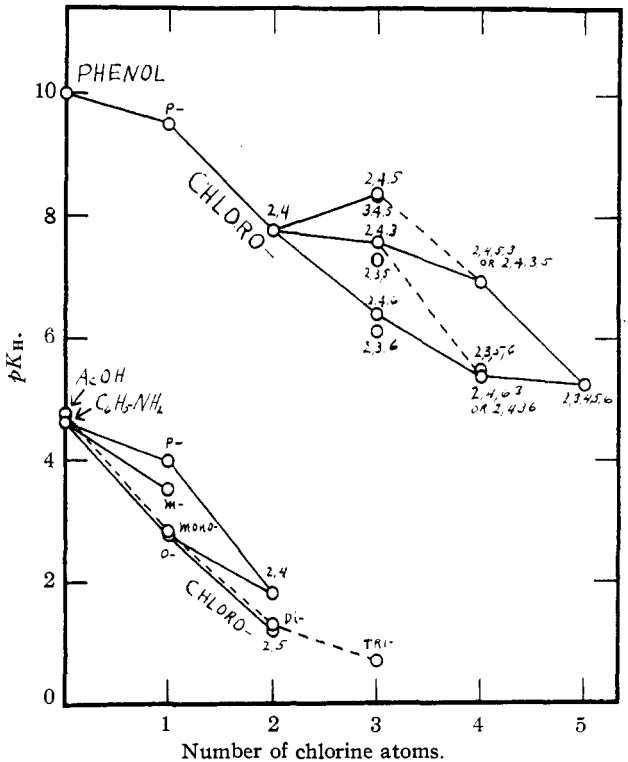

Fig. 5.—Effect of chlorine on strength of phenol, acetic acid and aniline: ordinates, pK_H; abscissas, no. of chlorine atoms.

Financial aid from the Milton Fund of Harvard University and the Research Fund of the University of Wisconsin is gratefully acknowledged, as is the kindness of many workers in the organic chemistry Laboratory of this University, who have supplied purified specimens of bases.

Summary

1. First determinations have been made of the ionization constants of thirty-eight organic derivatives of ammonia, and the constants of twenty-two bases have been redetermined as a control.

[11] See also Halford, THIS JOURNAL, **53**, 2939, 2944 (1931); Conant and Wheland, *ibid.*, **54**, 1213–1221 (1932).

2. One of the bases studied (guanidine) is stronger than any other for which a constant has been given.

3. The temperature coefficient of the constant K_w/K_B has been determined for six bases of different strength and found to vary in a regular manner with the base strength.

4. The effect of substituents on the strength of bases has been shown to be strictly comparable to their effects on the strength of acids.

5. Attention is directed for the first time to the effect of two ethyl groups in enhancing base strength.

6. Many other special effects have been exhibited by means of tables and diagrams.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE BUREAU OF MINES, U. S. DEPARTMENT OF COMMERCE]

THEORY OF THE ERROR OF ACID–BASE TITRATION[1]

BY PAUL S. ROLLER[2]

RECEIVED MARCH 31, 1932 PUBLISHED SEPTEMBER 5, 1932

The origin of the error of acid–base titration lies in the finite sensitivity of the end-point indicator. For a given sensitivity, the magnitude of the titer error increases with decrease in rate of change of P_H at the end-point. A weak acid is thus less accurately titrated than a strong one.

Formulation of the titer error permits one to predict the accuracy and limiting conditions of titration without laborious experimental trial and error. Furthermore, by comparison of the actual with the theoretical error, it can be decided whether or not complications that are not considered in the ideal case, such as side reactions, indicator decomposition, adsorption, etc., play a part.

In this paper formulations are presented for the theoretical titer error of the acid–base colorimetric and electrometric titration. For the latter the condition of the appearance of an inflection point and the magnitude of its deviation from the stoichiometric point are given. Owing to the practical utility of the results these are presented in their final form; at the end of the paper derivation is made for a simple case as illustrative of the general method.

Previous Results

McCoy[3] expressed the error in titrating a weak acid by a strong base with phenolphthalein as indicator. Noyes[4] and Tizard and Boeree[5] have

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[3] McCoy, *Am. Chem. J.*, **31**, 512 (1904).

[4] Noyes, THIS JOURNAL, **32**, 815 (1910).

[5] Tizard and Boeree, *J. Chem. Soc.*, **119**, 132 (1921).