pared by benzoylation of 5-amino-8-hydroxyquinoline showed no depression. Moreover, by hydrolysis with hydrochloric acid (20%) the formation of benzoic acid could be ascertained by the mixed melting point method.

Anal. Subs., 3.066: N_2, 0.290 (24°, 766 mm.). Calcd. for $C_{16}H_{12}O_2N_2$: N, 10.61. Found: N, 10.63.

Acid sulfate gave yellow columns from alcohol; m. p. 221–222° (decomp.).

8-Benzoyloxyquinoline.—The benzoylation of 8-hydroxyquinoline with benzoyl chloride was carried out in the presence of pyridine in the cold; yield, 90% of the theoretical after recrystallization. It forms in colorless tables from alcohol; m. p. 122–122.5°.

This compound was prepared first by Bedall by the interaction of 8-hydroxyquinoline and benzoyl chloride at a high temperature; he found a melting point of 118–120° for his product.[3]

Anal. Calcd. for $C_{16}H_{11}O_2N$: N, 5.62. Found: N, 5.54.

The hydrochloride was obtained by treating an ice cold ethereal solution of the free base with dry hydrogen chloride gas. It forms in colorless needles; m. p. 124°. It is easily soluble in water.

Anal. Calcd. for $C_{16}H_{11}O_2N \cdot HCl$: HCl, 12.78. Found: HCl, 12.54.

On submitting this hydrochloride to a Friedel and Crafts reaction, benzoic acid and 8-hydroxyquinoline could be recovered and no condensation product could be isolated.

I hereby desire to express my hearty thanks to Professor Hata for the interest which he has kindly taken in this work and to Mr. C. Sone for his assistance in this investigation.

Summary

The preparation of 5-acetyl-, 5-chloro-acetyl- and 5-benzoyl-8-hydroxyquinoline has been reported.

TOKYO, JAPAN

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE DETERMINATION OF THE STRENGTH OF WEAK BASES AND PSEUDO BASES IN GLACIAL ACETIC ACID SOLUTIONS[1]

BY J. B. CONANT AND T. H. WERNER

RECEIVED JULY 17, 1930 PUBLISHED NOVEMBER 5, 1930

Previous papers of this series have shown that the titration of bases with strong acids in glacial acetic acid solution may be followed by means of the chloranil electrode. We have been interested in extending this study of weak bases to weak pseudo-bases of the type of triphenyl carbinol. It is only by the use of a solvent such as glacial acetic acid that these weak pseudo-bases can be studied and the oxidation–reduction systems composed of free radicals and halochromic salts can be investigated. Before continuing the study of these more strictly organic problems, it was necessary

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[3] Bedall and Fischer, *Ber.*, 14, 1367 (1881).

[1] This is Paper 4 in a series on Superacid Solutions. For earlier papers of this series, see THIS JOURNAL. 49, 3047, 3062 (1927); and 50, 2367 (1928).

to obtain more information in regard to the factors influencing the dissociation constants of weak bases in glacial acetic acid. From the earlier work it was clear that the neutral salt concentration was an important factor. For example, the shape of the titration curves obtained by Hall and Werner[2] clearly pointed to a marked effect of the changing ionic strength on the strength of the base being titrated.

We shall first present in this paper certain results obtained in a study of the effect of the ionic strength on dissociation constants of weak bases in glacial acetic acid solution. The results were obtained by two different methods. One was the electrochemical method using the chloranil electrode in exactly the manner previously described. The other method was to take advantage of the color changes which take place when crystal violet is further neutralized by the addition of strong acids. These changes have been studied in detail in water solution by Adams and Rosenstein.[3] Since the results obtained by the e. m. f. method with colorless bases, and by a spectrophotometric method with crystal violet, are closely related, they will be discussed together.

The results obtained with crystal violet may be considered first. Adams and Rosenstein have proved that the change of color of this substance from violet through blue and green to yellow on adding strong acid, is due to the formation of the green and yellow ions which correspond to the addition of one and two protons, respectively, to the violet ion, according to the equations

$$\underset{\text{violet}}{B^+} + H^+ \rightleftharpoons \underset{\text{green}}{BH^{++}} \tag{1}$$

$$\underset{\text{green}}{BH^{++}} + H^+ \rightleftharpoons \underset{\text{yellow}}{BH_2^{+++}} \tag{2}$$

One is thus in a position to evaluate the equilibrium constants for the first and second reactions written above (K_1' and K_2') from spectrophotometric data. Actually, the values of K_2' are subject to a much greater experimental error and the agreement among them we found to be unsatisfactory, and the change of this constant with change in ionic strength was irregular, for reasons which are not entirely clear. For these reasons we shall attempt to interpret only the changes of K_1' with change of ionic strength, giving only an approximate value for K_2'.

Briefly, the method consisted in measuring the extinction coefficients of solutions of crystal violet in buffer solutions of definite ionic strength and measured $P_{\mathrm{H}}^{(\mathrm{HAc})}$. The concentration of dye was so small (4×10^{-6} to 2×10^{-6} molar) that its contribution to the ionic strength could be neglected. The extinction coefficient was measured at intervals of 10 mμ from 470 to 680. From the curves thus obtained with solutions which

[2] Hall and Werner, This Journal, 50, 2367 (1928).

[3] Adams and Rosenstein, *ibid.*, 36, 1452 (1914).

varied from violet ($P_{\text{H}}^{(\text{HAc})}$ + 4.75) to yellow (−3.96) through blue and green, it is possible to obtain by a process of trial and error the fundamentals corresponding to the extinction coefficients of the violet, the green and the yellow forms (B^+, BH^{++} and BH_2^{+++}). As a first approximation, the molecular extinction coefficients of crystal violet in 3 molar pyridine in glacial acetic acid ($P_{\text{H}}^{(\text{HAc})}$ + 4.75) were used for the fundamentals of the violet form and those for the yellow were taken from a 0.05 molar perchloric acid solution in glacial acetic acid. Beyond 540 mμ the absorption due to the yellow species, even if present in large amounts, is practically negligible. Therefore by studying a green solution (by using the appropriate buffer) it is possible to obtain a rough approximation of the green fundamental from the assumed violet fundamental. Finally, the three fundamentals were adjusted by a trial and error method so that the absorption curves obtained with all the fifty solutions yielded satisfactory agreement on the assumption of a certain composition for each solution. Three typical curves are shown in Fig. 1 and the fundamentals finally chosen are given in Table I. It may be noted that the equation for the extinction coefficient of a particular solution at a particular wave length is

$$V\epsilon_v + G\epsilon_G + Y\epsilon_y = \epsilon$$

where ϵ_v, ϵ_G and ϵ_y are the fundamentals and V, G and Y the fraction of the material present in the violet, green and yellow forms. Since there was no evidence of a colorless form, the sum of those fractions was taken as one. The fading, noted by Adams and Rosenstein, which was due to hydrolysis, was not evident in our work because the amount of water present was negligible. The algebraic solution of the above equation is impossible but satisfactory results may be obtained by the laborious trial and error method just described.

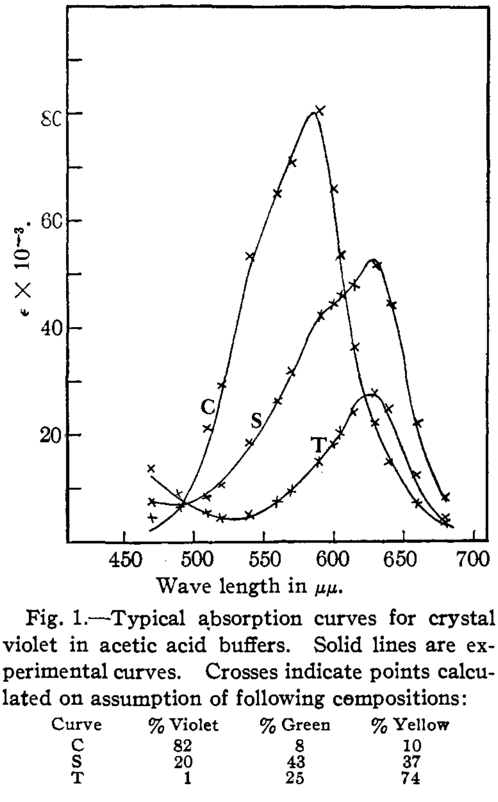

Fig. 1.—Typical absorption curves for crystal violet in acetic acid buffers. Solid lines are experimental curves. Crosses indicate points calculated on assumption of following compositions:

Curve	% Violet	% Green	% Yellow
C	82	8	10
S	20	43	37
T	1	25	74

Expressed logarithmically, the mass law equations for the two equilibria are

$$pK_1' = P_{\mathrm{H}}^{(\mathrm{HAc})} - (\log V - \log G) \qquad (1a)$$
$$pK_2' = P_{\mathrm{H}}^{(\mathrm{HAc})} - (\log G - \log Y) \qquad (2a)$$

The data obtained in the measurements of the $P_{\mathrm{H}}^{(\mathrm{HAc})}$ values are summarized in Table II and the results of the spectrophotometric measurements in Table III.

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS × 10^{-3}

Wave length	Crystal violet in 0.05 *M* $HClO_4$ in HAc	Crystal violet in 3 *M* pyridine in HAc	Fundamentals chosen for Violet form	Green form	Yellow form
470	19.0	3.01	2.45	...	19.0
490	12.4	8.16	9.40	...	12.8
510	6.15	20.7	25.0	2.0	6.5
520	4.20	31.9	35.0	5.0	4.2
540	1.50	61.0	63.8	13	1.7
560	0.42	77.0	76.6	26	0.5
570	.18	82.7	83.0	36	.18
590	.028	93.2	93.2	56	.028
600	.005	81.3	74.0	69	.005
605	...	68.2	58.0	80	...
615	...	40.8	35.0	95	...
630	...	13.8	16.2	112	...
640	...	7.10	8.47	100	...
660	...	3.20	4.02	50	...
680	...	2.50	2.60	18	...

TABLE II

MEASUREMENTS OF BUFFERS

(a) Urea–Sulfuric Acid Buffers

Soln.	Concn. of base, mole/liter	% Neutral with acid	$P_{\mathrm{H}}^{(\mathrm{HAc})}$	Ionic strength, μ	$\sqrt{\mu}$	pK' of base
U1	0.05	6	0.00	0.003	0.055	−1.20
U2	.20	6	+ .37	.012	.110	−0.83
U3	.05	32	− .54	.016	.127	− .87
U4	.20	14	+ .20	.028	.167	− .59
U5	.05	75	−1.00	.0375	.193	− .52
U6	.20	32	−0.03	.064	.253	− .36
U7	.20	50	− .33	.100	.316	− .33
U8	.20	75	− .80	.150	.387	− .32

(b) Urea–Perchloric Acid Buffers

Soln.	Concn. of base, mole/liter	% Neutral with acid	$P_{\mathrm{H}}^{(\mathrm{HAc})}$	Ionic strength, μ	$\sqrt{\mu}$	pK' of base
U12	0.00025	40	−0.51	0.0001	0.010	−0.69
U13	.003	50	−1.25	.0015	.039	−1.25
U14	.05	7.2	−0.32	.0036	.060	−1.43
U15	.05	13	− .58	.0065	.080	−1.41
U16	.05	39	− .90	.0195	.140	−1.09
U17	.05	50	−1.12	.025	.158	−1.12
U18	.20	45	−0.52	.09	.300	−0.61
U19	.30	50	− .46	.15	.387	− .46

TABLE II (*Concluded*)

Soln.	Concn. of base, mole/liter	% Neutral with acid	$P_H^{(HAc)}$	Ionic strength, μ	$\sqrt{\mu}$	pK' of base
	(c) Acetoxime–Sulfuric Acid Buffers					
A1	0.00025	40	−0.25	0.0001	0.01	−0.43
A2	.025	40	+ .21	.01	.10	+ .03
A3	.10	40	+ .61	.04	.20	+ .43
A4	.10	80	− .20	.08	.283	+ .40
A5	.10	80	− .24	.08	.283	+ .36
A6	.30	65	+ .42	.195	.44	+ .69

TABLE III

SUMMARY OF MEASUREMENTS OF DISSOCIATION CONSTANTS OF CRYSTAL VIOLET FROM SPECTROPHOTOMETRIC DATA AT 25°

Soln.	Color of solution	$\sqrt{\mu}$	$P_H^{(HAc)}$	Fraction of material as			Concn. of crystal violet $\times 10^6$	pK_1'	pK_2'
				Violet	Green	Yellow			
	(a) Urea–Sulfuric Acid Buffers								
U2	Blue-violet	0.110	+0.37	0.755	0.22	0.025	1.96	−0.17	−0.57
U4	Blue	.167	+ .20	.440	.40	.16	1.96	+ .16	− .20
U1	Blue-violet	.055	.00	.72	.17	.11	1.96	− .63	− .14
U6	Blue-green	.253	− .03	.17	.45	.38	3.92	+ .39	− .10
U3	Green-blue	.127	− .54	.17	.45	.38	1.96	− .12	− .61
U8	Green	.387	− .80	.004	.132	.864	3.92	+ .72	+ .02
U5	Yellow-green	.193	−1.00	.015	.285	.70	3.92	+ .28	− .61
	(b) Urea–Perchloric Acid Buffers								
U14	Blue	0.060	−0.32	0.37	0.40	0.23	1.96	−0.29	−0.56
U12	Light blue	.010	− .51	.20	.40	.40	1.96	− .21	− .51
U18	Yellow-green	.300	− .52	.02	.32	.66	3.92	+ .68	− .20
U15	Green-blue	.080	− .58	.20	.465	.335	1.96	− .21	− .72
U16	Yellow-green	.140	− .90	.025	.33	.645	3.92	+ .22	− .61
U17	Yellow-green	.158	−1.12	.01	.25	.74	3.92	+ .28	− .65
	(c) Acetoxime–Sulfuric Acid Buffers								
A3	Blue	0.20	+0.61	0.59	0.26	0.15	1.96	+0.25	+0.37
A6	Green-blue	.44	+ .42	.20	.43	.37	1.96	+ .75	+ .35
A2	Blue	.10	+ .21	.63	.22	.15	1.96	− .25	+ .04
A4	Green-blue	.283	− .20	.13	.46	.41	1.96	+ .35	− .25
A1	Violet	.01	− .25	.82	.08	.10	1.96	−1.26	− .15

Throughout this paper we have used the same arbitrary convention in regard to the placing of the $P_H^{(HAc)}$ scale as that used in the previous papers of this series. The actual numerical values of the *pK's* are therefore given in terms of the zero point of that scale. The uncertainty in the reproducibility of the P_H values is probably about ±0.02.

The data given in Table III are plotted in Fig. 2. The smooth curves correspond to equations relating pK' and $\sqrt{\mu}$ developed from the fundamental Debye–Hückel Equation 3.

$$-\log \gamma = \frac{Az^2\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \tag{3}$$

Taking the dielectric constant of the medium as 10 and the temperature as 25°, the values of A and B are found to be 11.15 and 0.921×10^8. Substituting we obtain Equation 4

$$-\log \gamma = \frac{11.15\, z^2 \sqrt{\mu}}{1 + 0.921 \times 10^8 a \sqrt{\mu}} \tag{4}$$

Defining the term pK_1 by Equation 5 and substituting the value of $-\log \gamma$ from (4) with appropriate values for z (+1 for z_1 and +2 for z_2), Equation 6 results

$$pK_1 = pK_1' - \log \frac{\gamma_1}{\gamma_2} \tag{5}$$

$$pK_1 = pK_1' - \frac{33.5 \sqrt{\mu}}{1 + 0.921 \times 10^8 a \sqrt{\mu}} \tag{6}$$

The denominator of the fraction in Equation 6 may be taken as unity for small values of $\sqrt{\mu}$. The resulting equation defines the limiting slope for the change of pK_1' in dilute solutions; this is shown by line E, Fig. 2. For purposes of comparison, the corresponding slope in aqueous solutions is shown by line A. Applying the limiting equation to the values for pK_1' obtained in the more dilute solution we estimate pK_1 as -1.7. Substituting this value in Equation 6, and taking "a" as 1.3×10^{-7}, an equation corresponding to Curve B results. Curves C and D were obtained by choosing values of "a" of 1.24 and 1.16×10^{-7}. In deriving Equation 4 the value of the dielectric constant for acetic acid at 25° was taken as 10; the recent measurements of Smyth[4] indicate that the correct value is more nearly 6 for 100% acetic acid. However, since the effect of the presence of salts and a small amount of water (the acetic acid employed in this work melted at 16.4° and contained

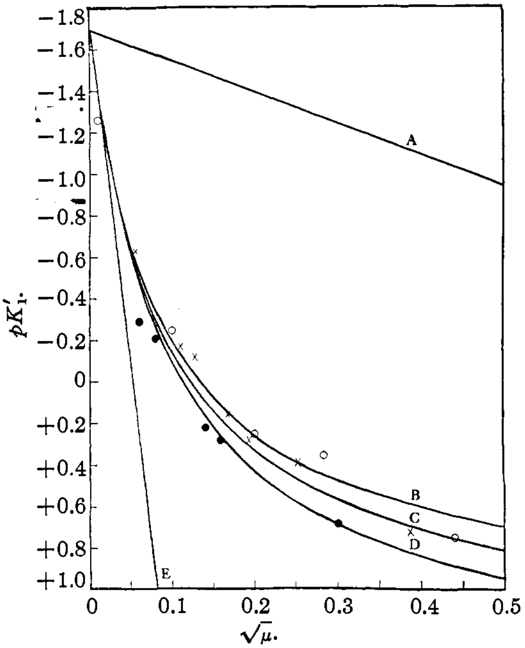

Fig. 2.—Change of pK'_1 for crystal violet with change in ionic strength. A, Theoretical slope for very dilute water solutions; E, theoretical slope for very dilute solutions in glacial acetic acid; B, ○, in acetoxime–sulfuric acid buffers; C, ×, in urea–sulfuric acid buffers: D, ●, in urea–perchloric acid buffers.

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[4] Smyth, This Journal, **52**, 1825 (1930).

about 0.2% of water) is uncertain, we have not thought it worth while to carry through another set of calculations using the dielectric constant of 6. The smaller value would merely give a steeper limiting slope and a different value of "a" (essentially an arbitrary constant) would be required in fitting the equation to the experimental points.

The tremendous effect of change of ionic strength on the value pK'_1 for crystal violet is evident from Fig. 2. This effect is particularly large in this case, of course, because of the fact that the reaction involves the addition of a proton to a singly charged positive ion with the formation of the doubly charged positive ion. The limiting slope of the Debye theory corresponds to a change of more than 2 P_H units for an increase of $\sqrt{\mu}$ from 0 to 0.05. This is about twenty times the corresponding effect in water, due to the extremely low dielectric constant of glacial acetic acid. However, as a matter of actual fact, the experimental points show a departure from the theoretical limiting slope long before this value is reached, and the total change of pK'_1 from the limiting value at $\mu = 0$ to $\sqrt{\mu} = 0.5$ is about 2.6 P_H units.

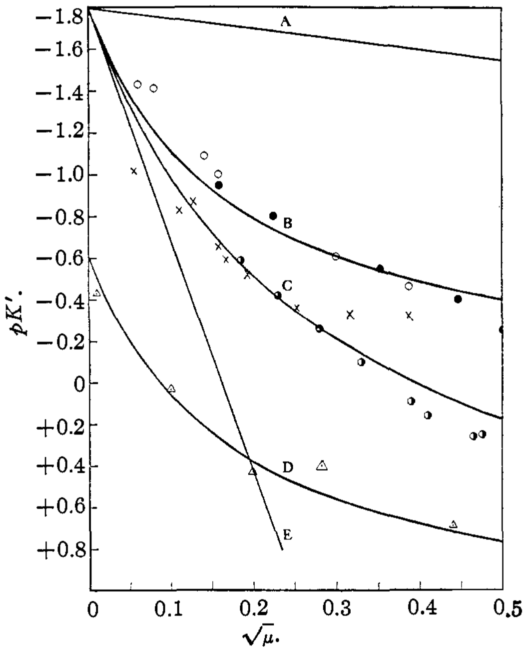

Fig. 3.—Change of pK' for urea and acetoxime with change in ionic strength. A, Theoretical slope for very dilute water solutions; E, theoretical slope for very dilute solutions in glacial acetic acid; B, ○, ●, urea–perchloric acid; C, × ◑, urea–sulfuric acid; D, △, acetoxime–sulfuric acid; ◑, effect of neutral salt (trimethylammonium p-toluene sulfonate) on pK' of urea half neutralized with H_2SO_4; ● urea–perchloric acid points from data by Hall and Werner.

The results shown in Fig. 3, which represent the effect of changing ionic strength on the values of pK' for urea and acetoxime, reveal a situation similar to that discussed in the preceding paragraph, except that the limiting slope is here only one-third of that found in the case of crystal violet since the reaction involves the formation of a singly charged ion from a neutral molecule. Neither these results nor those obtained with crystal violet are sufficiently accurate to give a very significant extrapolated value for pK_1 since it is very difficult to obtain measurements in solutions of low ionic strength. In fact, the first value in Section b of Table II has been omitted from Fig. 3 since it is clearly out of line with the other results, presumably because of the difficulties of measuring significant e. m. f.'s with very dilute solutions. In the case of the crystal violet measurements, which were made spectrophotometrically, the solution may be very dilute with respect to the base, but one is dependent on electrical measurements for the $P_H^{(HAc)}$ values of the buffer solutions which must, therefore, be relatively concentrated.

Three different sets of data were used in plotting Fig. 3, as indicated by the symbols. The measurements of the $P_H^{(HAc)}$ values of the buffers employed for the crystal violet work comprised one set; these data are given in Table II. Another set of facts was obtained by adding measured increments of a molar solution of $(CH_3)_3NHSO_3C_6H_4CH_3(p)$ in glacial acetic acid to a 0.05 molar solution of urea in the same solvent half neutralized with sulfuric acid. The ionic strength was calculated as the sum of that contributed by the urea salt and the added neutral salt. The $P_H^{(HAc)}$ was measured in the usual way and since the urea was half neutralized these numbers corresponded directly to the pK'. The third set of values was calculated from the titration of urea with perchloric acid given by Hall and Werner.[2] The value of pK for urea was taken as -1.8 by extrapolation by means of the limiting law Debye equation (Curve E). Curves B and C were drawn from the application of Equations 4 and 5 ($z_1 = 0$, $z_2 = +1$) and "a" being taken as 0.65×10^{-7}, and 0.4×10^{-7}, respectively; the equations for Curves B and C were thus

$$pK' = pK + \frac{11.15\sqrt{\mu}}{1 + 5.98\sqrt{\mu}} \tag{7}$$

and

$$pK' = pK + \frac{11.15\sqrt{\mu}}{1 + 3.68\sqrt{\mu}} \tag{8}$$

Curve D for acetoxime was the same as Curve B, the extrapolated value for pK being taken as -0.6.

It is evident from the data summarized in Figs. 2 and 3 that in the more concentrated solutions there are specific effects depending on the nature of the neutral salt. These effects are larger than the corresponding effects in water because of the low dielectric constant of acetic acid. The agreement between the urea-perchloric acid points from the data of Hall and Werner and from Table II is gratifying as showing the reproducibility of our methods. It is clear that both the nature of the cation and anion of the neutral salt are important (divergence of the points on Curves C and D, Fig. 1, and B and C, Fig. 2). The application of these facts to the use of indicators in glacial acetic acid is evident and until the very large "salt effect" with each compound is carefully plotted, conclusions drawn from the use of indicators are only very approximate.

We have been particularly concerned in reducing to a practical working basis our knowledge of strong acids and weak bases in glacial acetic acid with the idea of constructing buffer solutions. The information which we have now obtained from the study of crystal violet, urea and acetoxime, shows clearly the great importance of the ionic strength. In comparing a series of results in buffer solutions, the ionic strength must be constant. If possible, the same neutral salt should be used in every case but even if this is not possible it is better to make all the solutions of the same ionic strength than to neglect this factor. Variations as great as a *P*H unit might perhaps be caused by a difference in the nature of the neutral salt, although most of the effects recorded in this paper are only of the order of a few tenths of a *P*H unit.

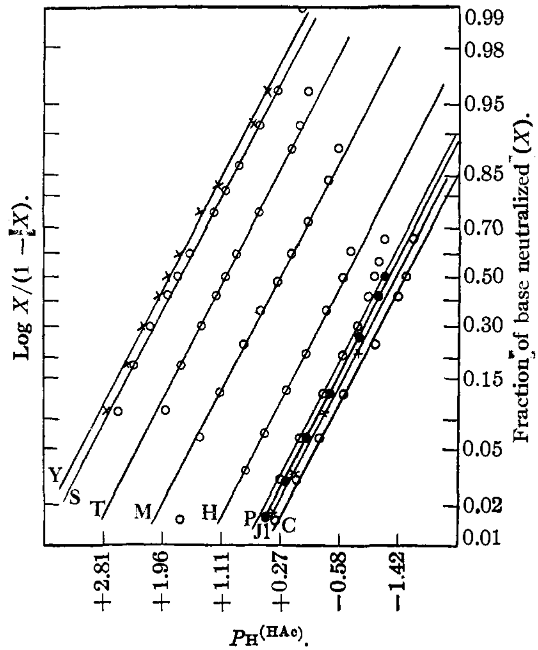

Fig. 4.—Titration curves of bases with sulfuric acid at ionic strength of 0.2 (trimethyl ammonium *p*-toluene sulfonate) plotted on a "Logistic Grid." C, Triphenyl carbinol; I, dianisylcarbinol; J, dianisalacetone; P, acetanilide; H, diphenylanisylcarbinol; M, urea; T, acetoxime; S, *o*-chloro-aniline; Y, phenylxanthanol.

If the ionic strength is kept constant by employing a relatively large amount of a neutral salt, satisfactory values of pK' can be obtained in a series of experiments. This is illustrated by the results summarized in Table IV for crystal violet in solutions of μ = 0.20. The titration curves of nine bases (including three pseudo bases discussed below) obtained in solutions of μ = 0.20 are plotted in Fig. 4. Since the ionic strength due to the neutral salt (trimethylammonium *p*-toluene sulfonate) is here large compared to the concentration of base (0.05 molar), the increase of ionic strength during the titration is negligible. For this reason the points lie much closer to the theoretical curve than was the case in the investigation by Hall and Werner where no neutral salt was employed. The neutral salt employed in the experiments recorded in Table IV was triethylammonium perchlorate. The values of pK' for urea given in Col. 4 of Table IV vary only slightly more than the probable experimental error; the average value −0.35 ($\sqrt{\mu}$ = 0.446) is to be compared with the values of −0.42 and +0.1 obtained at the same ionic strength but with the ionic strength contributed by urea perchlorate and trimethylammonium *p*-toluene sulfonate, respectively (Fig. 3). The specific effect of the different neutral salts is evident.

TABLE IV

CONSTANTS FOR CRYSTAL VIOLET OBTAINED WITH BUFFER SOLUTIONS OF CONSTANT IONIC STRENGTH

Temp., 25.0°; μ, 0.200; urea–sulfuric acid mixture (concn. of urea + urea ion = 0.05 molar) with the addition of triethyl ammonium perchlorate.

Base neut., %	Cc. of 0.3 *M* neutral salt in 50 cc. of buffer	P_H(HAc)	pK' of urea	Concn. of crystal violet, moles per liter $\times 10^6$	Fraction of material as			pK'_1	pK'_2
					Violet	Green	Yellow		
95	25.7	−1.22	....	3.92	0.0012	0.105	0.894	0.72	−0.29
75	27.3	−0.74	−0.26	3.92	.007	.220	.773	.76	− .19
50	29.4	− .31	− .31	3.92	.034	.362	.604	.72	− .09
40	30.3	− .19	− .37	3.85	.06	.41	.53	.64	− .08
32	31.0	− .07	− .40	3.77	.08	.44	.48	.67	− .03
14	32.5	+ .42	− .37	1.96	.23	.48	.29	.74	+ .20
6	33.1	+ .80	− .40	1.96	.46	.36	.18	.69	+ .50
0	33.6	+1.59	....	1.96	.88	.11	.009	.69	+ .50

As mentioned earlier in this article, the determination of pK'_2 for crystal violet was not satisfactory. The results have already been given in Tables III and IV. If one plots pK'_2 against $\sqrt{\mu}$ a rather irregular distribution of the points is obtained, the values being more negative in the more dilute solution, as would be expected. The range of values obtained at constant ionic strength is large and we are inclined to attribute the spread to experimental error in determining the percentage of yellow form with its very low extinction coefficient, although there is a regular trend in the data for which we have no explanation.

In connection with the comparison of the dissociation constants of weak bases in water and in acetic acid, it is interesting to consider the results we have obtained with crystal violet and those of Adams and Rosenstein. The values of pK'_1 and pK'_2 in aqueous solution are given by these authors as +1.94 and +1.15, and we may assume that these are also the values for pK_1 and pK_2 in water. Our extrapolated values are −1.7 and approximately -1.4, although the latter value can hardly be considered of much significance due to the difficulties connected with the measurement of pK'_2. Adams and Rosenstein's value for pK_1 is more positive by about 3.6 units than our value. Taking the value of pK for urea as -1.8 and comparing it with the value in water of about 0, we note that the latter is more positive by about two units. The contrast between water and acetic acid is less with urea than with crystal violet for the reason pointed out by Brönsted,[5] namely, that we are dealing with the reaction $B \longrightarrow BH^+$ instead of $B^+ \longrightarrow BH^{++}$. Any attempt to make correct adjustment between the P_H scale in water and acetic acid (if indeed an accurate adjustment is really conceivable),[6] will obviously have to wait until more data can be accumulated which will enable the value of the pK' for different acids and bases in both solvents to be extrapolated to infinitely dilute solution. For practical purposes in the immediate future, we shall continue to use the scale as originally defined, realizing its empirical nature but believing that the position of the zero expresses the qualitative difference between the behavior of solutions of strong acids in water and glacial acetic acid.

Pseudo Bases.—Four of the bases whose titration curves are plotted in Fig. 4 are pseudo bases which react according to the following equation:

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

These are triphenylcarbinol (C), dianisyl carbinol (I), diphenylanisylcarbinol (H), and phenylxanthanol (Y). It is clear that the titration method in glacial acetic acid provides for the first time a method of obtaining really significant values for the basic strength of these very weak pseudo bases. In order to be able to formulate the neutralization of these compounds in the same general scheme as that used for the other bases, we will consider the positive ion in the presence of water as an acid and write the equation

$$pK' = P_H - \log \frac{[BOH]}{[B^+]} + \log (\text{activity of the } H_2O) \qquad (9)$$

Because the compound BOH is a pseudo base, water is necessary for B^+ to be an acid. The strength of B^+ as an acid thus depends on the activity of the water in the solvent. When considering pseudo bases in solutions containing large quantities of water, the activity of the water may be taken as constant; Equation 9 then reduces to the usual form.

In this manner Kolthoff[7] and Lund[8] formulated their interesting results obtained with acetone–water solutions of the polymethoxytriphenyl carbinols. The apparent pK' of a pseudo base measured in acetic acid is a function of the activity of the water according to Equation 10.

[5] Brönsted, *Chem. Reviews*, **5**, 295 (1928).

[6] *Cf.* Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929).

[7] Kolthoff, This Journal, **49**, 1218 (1927).

[8] Lund, *ibid.*, **49**, 1346 (1927).

$$\text{App. value of } pK' = pK' - \log A_{H_2O} = P_H^{(HAc)} - \log \frac{[BOH]}{[B^+]} \qquad (10)$$

The glacial acetic acid used in the experiments reported in Fig. 4 melted at 16.6° and probably contained an amount of water less than that produced by the neutralization of the pseudo-base.[9] The pK' measurements corresponded to half neutralization of a 0.05 molar solution of the pseudo base so that the total water concentration may be taken as approximately 0.025 (mole fraction, 0.0014). If we assume that in such dilute solutions the activity of the water is equal to its molar concentration, we may approximate the values of pK' from the measured values by subtracting 1.6 units.

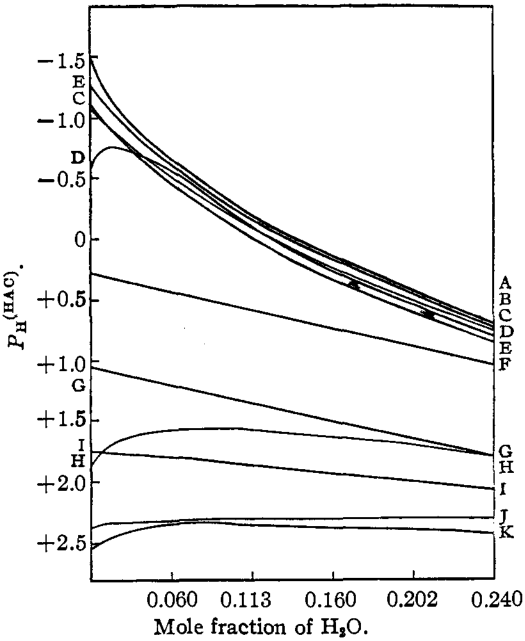

Fig. 5.—Effect of water on bases half neutralized with H_2SO_4. Ionic strength, 0.2. A, Triphenylcarbinol; B, α-naphthyldiphenylcarbinol; C, acetanilide and also dianisal acetone; D, diphenylanisylcarbinol; E, dianisylcarbinol; F, urea; G, acetoxime; H, phenylxanthanol; I, *o*-chloraniline; J, dinaphthoxanthanol; K, trianisylcarbinol.

If the concentration of water in glacial acetic acid is increased, the measured value of pK' will become more negative according to Equation 10. If this were the only factor involved, the $P_H^{(HAc)}$ value of an equimolecular mixture of BOH and B^+ should become more negative with increasing water content. However, the addition of water to any glacial acetic acid solution of an acid makes the $P_H^{(HAc)}$ value more positive, presumably because of the formation of the H_2OH^+ ion in increasing quantities. Two opposing effects are thus at work; in solutions of very negative $P_H^{(HAc)}$ values the second effect is so marked as to obscure the first entirely, while in all solutions it becomes the predominant factor after the mole fraction of water is about 0.060. The results shown graphically in Fig. 5 illustrate these conclusions. Solutions of a variety of bases (real and pseudo) were titrated with sulfuric acid to the midpoint and then a dilute solution of water added and the change of $P_H^{(HAc)}$ values recorded. The

[9] Kendall and Gross, This Journal, **43**, 1426 (1921); Webb, *ibid.*, **48**, 2265 (1926); Smyth, *ibid.*, **52**, 1824 (1930); all give 16.6° as the melting point of pure acetic acid.

ionic strength was 0.2 (the neutral salt was $(CH_3)_3NHSO_3C_6H_4CH_3$) and the initial concentration of the base 0.05 molar. Four pseudo bases, diphenylanisyl carbinol, phenylxanthanol, dinaphthoxanthanol and trianisylcarbinol, show a decrease and then a rise of $P_H^{(HAc)}$ values with increasing water concentration. With the very weak pseudo bases, triphenylcarbinol, α-naphthyldiphenylcarbinol and dianisylcarbinol, the effect cannot be detected since the decrease of proton activity due to the increased water content predominates from the start. All the real bases show a progressive increase in $P_H^{(HAc)}$ values, as would be expected.

The apparent values of pK' for the pseudo bases we have examined are given in Table V. These values are for 23 ± 1°, 0.05 molar solution of the base titrated with sulfuric acid, ionic strength, 0.2 and glacial acetic acid of m. p. 16.6°. The measure of the basicity by these numbers is independent of any assumptions about color and ionization. In order to evaluate pK, it will be necessary to take into account both the change of pK' with ionic strength and the activity of water in acetic acid. In the case of the stronger bases a further complication results from the fact that the weak second hydrogen of sulfuric acid may be involved; this tends to make the values of pK' too negative.[2] A sulfonic acid would be preferable for titrations of these strong pseudo bases. Further work along these lines is in progress in this Laboratory and the present results must be considered as preliminary. For this reason a discussion of the interesting relationships between structure and pK values will be postponed. It may be noted, however, that our value for trianisylcarbinol (4,4′,4″-trimethoxycarbinol) is +2.6, while the value found by Lund in 50% acetone and water is −0.77. Assuming that the apparent pK' value changes with ionic strength in the same way as with urea (-2 units $\mu = 0.2$ to $\mu = 0$) and that the comparison between water and glacial acetic acid is also the same ($pK^{(H_2O)} - pK^{(HAc)} = +2.0$), it is clear that the two effects cancel. The difference between our value of +2.7 and Lund's −0.77 (a total of 3.5 units) should be a measure of the difference in activity of the water in a 0.025 molar concentration in glacial acetic acid and in 50% aqueous acetone. No data appear to be

TABLE V

SUMMARY OF APPARENT pK' VALUES OF CERTAIN PSEUDO BASES AT 25° IN GLACIAL ACETIC ACID, M. P. 16.6°. BASES IN 0.05 MOLAR SOLUTION TITRATED WITH SULFURIC ACID $\mu = 0.2$ WITH $(CH_3)_3NHSO_3C_6H_4CH_3(p)$

Name	Formula	Apparent pK'
Triphenylcarbinol	$(C_6H_5)_3COH$	−1.47
α-Naphthyldiphenylcarbinol	$(C_{10}H_7)(C_6H_5)_2COH$	−1.25
Dianisylcarbinol	$(C_6H_4OCH_3)_2HCOH$	−1.14
Diphenylanisylcarbinol	$(C_6H_5)_2(C_6H_4OCH_3)COH$	−0.59
Phenylxanthanol	$(C_6H_4)_2O(C_6H_5)COH$	+1.91
Dinaphthoxanthanol	$(C_{10}H_6)_2OCHOH$	+2.40
Trianisylcarbinol	$(C_6H_4OCH_3)_3COH$	+2.56

available to check this but the direction of the effect is correct and the order of magnitude seems reasonable.

Experimental

(a) **Materials.**—The acetic acid was purified by repeated freezing of redistilled commercial synthetic acetic acid. The melting point was 16.4° except in the work with the pseudo bases when material of m. p. 16.6° was employed. Anhydrous perchloric acid was prepared from 60% aqueous acid and acetic anhydride as previously described. The solution of sulfuric acid in glacial acetic acid was prepared from 99.9% sulfuric acid. It was standardized by electrometric titration in glacial acetic acid with sodium acetate. The crystal violet employed was Dr. Grübler's "Höchst" brand. Its absorption spectrum was determined in aqueous solution and was found to be identical with that given by Adams and Rosenstein within our experimental error.

All the organic substances used in this work except the "neutral salts" are familiar compounds easily purified and characterized by their melting points; no description of them is therefore required. The neutral salts were prepared by passing the amine into a water solution of the acid, evaporating to dryness in vacuum and drying over phosphorus pentoxide. Both substances were colorless crystalline solids.

(b) **Apparatus.**—The spectrophotometer employed was a Keuffel and Esser color analyzer. Its adjustment was tested by means of a blue and yellow glass whose extinction coefficients over a wide range had been determined by the Bureau of Standards. The solution was placed in a 10-cm. glass cell with fused glass ends; a cell of the same length containing acetic acid was placed in the comparison beam. The temperature was kept at 25 ± 0.3°. Three readings were taken at each wave length and averaged.

The electrometric measurements were made with a cell similar to that previously used but so constructed that only 10 cc. instead of 50 cc. could be employed. It is shown in Fig. 6; a micro-buret was used in the titrations. The temperature was 23 ± 1°. The $P_{\rm H}^{(\rm HAc)}$ values were obtained from the measured e. m. f. (E) by the equation previously employed.

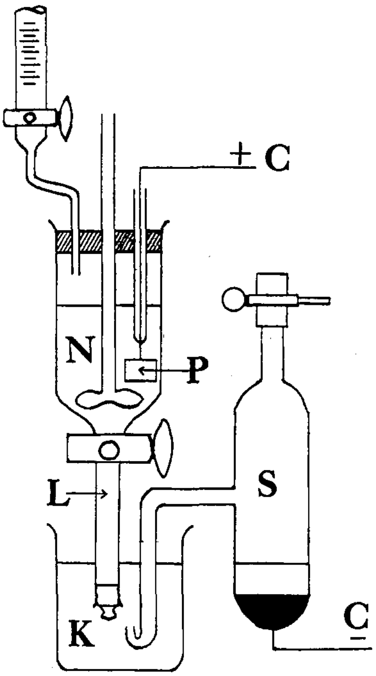

Fig. 6.—Cell for titrations in glacial acetic acid using chloranil electrode. S, Saturated calomel electrode; K, saturated KCl in water; L, LiCl in acetic acid; N, 10 cc. of solution to be measured; P, platinum electrode; C, connections to electrometer and potentiometer.

$$P_{\rm H}^{(\rm HAc)} = \frac{0.566 - E}{0.059}$$

Summary

1. A spectrophotometric study has been made of the acid–base equilibria in solutions of crystal violet in buffered glacial acetic acid solutions.

2. An electrometric study of a number of weak bases and pseudo bases in glacial acetic acid has revealed the large effect of changing ionic strength which was also noted in the spectrophotometric study.

3. The effect of added water on the apparent constants of a number of weak pseudo bases has been investigated and a method outlined for obtaining significant values for the relative basicity of the "halochromic" carbinols.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

V. THE CONDENSATION OF HYDROCARBONS BY ELECTRICAL DISCHARGE. COMPARISON WITH CONDENSATION BY ALPHA RAYS[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

RECEIVED JULY 18, 1930 PUBLISHED NOVEMBER 5, 1930

In a former paper[4] it has been shown that the condensation of ethane by electrical discharge in an ozonizer is in many ways similar to the same reaction when produced by the ionization due to the alpha particles from radon.[5] The experiments have now been extended to the gases methane, propane, butane and ethylene. It has been found *that there exists a similarity in the condensations as produced by the ionization due to α-particles and by electrical discharge in an ozonizer* for all the gases studied. It is the object of the present paper to describe these experiments and to discuss certain experimentally determined ratios which support the statement made. The experiments on ethane have been repeated with the new apparatus and confirm the former study. They are included for the sake of completeness and for comparison.

Experimental Procedure

The apparatus used to study these condensations is shown in Fig. 1 and consists of an all-glass pyrex ozonizer, a Liebig condenser and a manometer. The system as a whole is of the circuit type and a slight circulation was probably attained by the thermal siphon principle since the ozonizer would naturally heat up (to about 40°) during a run due to power losses and since the condenser kept the other leg of the system cold, by

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[1] This paper includes part of an investigation on "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum Research. Financial assistance has been received from the research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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[4] S. C. Lind and George Glockler, *Trans. Am. Electrochem. Soc.*, **52**, 37–46 (1927).

[5] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2335–2351 (1926).