

dine and acetic anhydride. It crystallized from five parts of 50% alcohol in long colorless needles melting at 92° (corr.) to a colorless oil. Its specific rotation was -24.9° (0.3570 g. in 10 cc. of chloroform in a 1-dm. tube rotated 0.89° to the left) after recrystallization to constancy.

*Anal.* Calcd. for C<sub>19</sub>H<sub>28</sub>O<sub>12</sub>: C, 50.87; H, 6.30. Found: C, 50.81; H, 6.37.

*d*-[ $\alpha$ -Galaheptose] Benzyl Mercaptal.—A solution of 5 g. of  $\alpha$ -galaheptose monohydrate in 10 cc. of concd. hydrochloric acid was shaken with 10 cc. of benzyl mercaptan for ten minutes, when it set to a paste. After standing overnight at room temperature the solid was filtered, washed with 95% alcohol and dried, yield, quantitative. The mercaptal may be recrystallized readily from 75 parts of 95% alcohol, separating in small glistening plates, melting at 191° (corr.) and rotating +30.3° in pyridine (0.2212 g. in 10 cc. in a 1-dm. tube rotated 0.67° to the right).

*Anal.* Calcd. for C<sub>21</sub>H<sub>28</sub>O<sub>6</sub>S<sub>2</sub>: S, 14.56. Found: S, 14.50.

Hexaacetyl *d*-[ $\alpha$ -Galaheptose] Benzyl Mercaptal.—A solution of 5 g. of mercaptal in 25 cc. of pyridine was treated with 25 cc. of acetic anhydride, allowed to stand overnight at room temperature and the acetate precipitated by pouring the solution over crushed ice. The compound crystallizes from 10 parts of 95% alcohol in clusters of elongated, very thin terminated plates, melting at 120° (corr.) and rotates -10.6° (0.2633 g. in 10 cc. in a 1-dm. tube rotated 0.28° to the left) in chloroform.

*Anal.* Calcd. for C<sub>38</sub>H<sub>40</sub>O<sub>12</sub>S<sub>2</sub>: S, 9.26. Found: S, 9.14.

Hexabenzoyl *d*-[ $\alpha$ -Galaheptose] Benzyl Mercaptal.—A solution of 3 g. of mercaptal in 25 cc. of pyridine was treated dropwise with 11.5 g. of benzoyl chloride. The

mixture became warm, developed a red color and soon became a mush of glistening crystals. The next day the mass was poured upon crushed ice, stirred and a red crystalline meal gradually formed. This was filtered off and recrystallized from 100 parts of 95% alcohol, the benzoate separating in clusters of colorless small prisms. The pure substance melts at 129° (corr.) and rotates -48.1° in chloroform (0.2950 g. in 10 cc. in a 1-dm. tube rotated 1.42° to the left).

*Anal.* Calcd. for C<sub>63</sub>H<sub>52</sub>O<sub>12</sub>S<sub>2</sub>: S, 6.02. Found: S, 6.03.

### Summary

1. *d*-[ $\alpha$ -Galaheptose] has been obtained in crystalline condition as the monohydrate of its beta form.

2. The rotational behavior of solutions of crystalline *d*-[ $\alpha$ -galaheptonic] acid has been studied.

3. Methyl and ethyl glycosides of [*d*- $\alpha$ -galaheptose] and their acetates have been obtained in pure condition.

4. The benzyl mercaptal, its acetate and benzoate have been prepared and described.

5. Attention has been called to the parallelism of physical and chemical properties, as well as rotational behavior, of substances of configurationally related structure in the sugar group, as illustrated from substances of the mannose and  $\alpha$ -galaheptose series.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Determination of Ionization by Ultraviolet Spectrophotometry: Its Validity and its Application to the Measurement of the Strength of Very Weak Bases<sup>1</sup>

By LEO A. FLEXSER,<sup>2</sup> LOUIS P. HAMMETT AND ANDREW DINGWALL

It has been amply demonstrated that most organic oxygen compounds are bases of the same kind as ammonia or aniline, but of a much less pronounced basicity.<sup>3</sup> Quantitative knowledge of the strength of these very weak bases is practically non-existent,<sup>4</sup> yet is of crucial importance

(1) This article is based upon the dissertation submitted by Leo A. Flexser to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1935. The material was presented at the New York meeting of the American Chemical Society, April, 1935. A preliminary Communication appeared in THIS JOURNAL, **56**, 2010 (1934).

(2) University Fellow in Chemistry, 1934-1935.

(3) (a) Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908); (b) *ibid.*, **65**, 41 (1908); (c) Hammett and Deyrup, THIS JOURNAL, **55**, 1900 (1933).

(4) Hammett, *Chem. Rev.*, **13**, 61 (1933).

for the understanding and interpretation of the phenomena of acid catalysis. One of the most promising methods for obtaining these data<sup>4</sup> involves the measurement of the extent of ionization of the base (that is to say, the extent of conversion of the base B to the cation or conjugate acid BH<sup>+</sup>) in mixtures of sulfuric acid and water. Such measurements of extent of ionization have previously been made by the method of visual colorimetry;<sup>5</sup> we have now made the rather obvious extension<sup>4</sup> to spectrophotometry in the ultraviolet for cases where there is no visible change in color.

(5) (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) Hammett and Paul, *ibid.*, **56**, 827 (1934); (c) Hammett, *Chem. Rev.*, **16**, 67 (1935).

The simple fact that most organic acids and bases have absorption spectra which differ materially from those exhibited by the corresponding anions or cations has been so beclouded in the discussions of indicator theory that there has even been room to doubt the possibility of determining ionization by measurements of the absorption spectra of simple acids and bases. The method has indeed been successfully applied by Stenström and co-workers<sup>6</sup> to the measurement of the ionization of phenol, but they reported the method inapplicable to the ionization of benzoic acid, and no one else seems to have considered even the possibility of such measurements. Before attempting the determination of unknown constants we have therefore first verified the method on the constants in dilute aqueous solution of benzoic acid, dinitrophenol and aniline, which are known from more familiar methods of measurement.

### Experimental

**Apparatus.**—All apparatus was calibrated either directly or indirectly against apparatus certified by the Bureau of Standards.

The absorption spectra were determined with a Hilger quartz sectorphotometer<sup>7</sup> and E-316 spectrograph using as a source of light a 25,000-volt condensed spark between tungsten electrodes in air. The ultraviolet spectrum down to 2000 Ångström units could be recorded on a single 10.2 by 25.4 cm. photographic plate. The wave length scale was calibrated by means of a copper arc and found to be correct within the error of visually determining match points, *i. e.*, better than 5 Å. throughout the ultraviolet and better than 10 Å. between 4000 and 5000 Å.

Moving pictures taken of the original photometer while the sectors were rotating showed that erratic slipping took place between the belts and the rotating sector disks. This was eliminated by cutting gears into the disks, and meshing them with one another. The upper and lower sectors could both be varied and were used on alternate exposures so that any error arising from initially imperfect matching of the upper and lower halves of the spectrum was automatically canceled out. The angular apertures of the sectors were measured and found to be correct within 5% up to sector settings of  $-\log T = 1.3$ . The sectors were never used above settings of 1.2 and since most settings were taken in half-unit steps on the less crowded portions of the scale between 0 and 1.0, it is probable that the error is in the neighborhood of 3%. The spark stand, photometer, and spectrograph were mounted on a heavy iron casting, which gave such stability that the instruments would keep their relative positions for several months.

As a check on the set-up, the percentage transmission of a piece of blue glass was measured and compared with

(6) (a) Stenström and Reinhard, *J. Phys. Chem.*, **29**, 1477 (1925); (b) Stenström and Goldsmith, *ibid.*, **30**, 1683 (1926).

(7) Twyman and Allsopp, "The Practice of Spectrophotometry," Adam Hilger, Ltd., London, 1934.

the results obtained by the Bureau of Standards for the same piece of glass by an entirely different method, results herewith.

Wave length, Å.	% Transmission	
	Obsd.	Bureau report
5200	80.0	80.6
5600	55.0	58.0
6000	34.0	34.5
6400	17.7	18.0

The agreement is surprisingly good considering the various sources of error inherent in the method.<sup>8</sup>

Two quartz cells were used, one to contain the solvent and the other the solution. The solvent cell was placed in front of the upper sector, the solution cell in front of the lower sector and settings of  $-\log T = 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0$  and  $1.2$  were taken on the upper sector. The cells were then interchanged and settings of  $0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95$  and  $1.1$  taken on the lower sector. A blank setting of 0 on both sectors with the cells removed was taken at the beginning and end of each plate as a check on the instrumental adjustment.

Although several types of cells were used, the most satisfactory were made by clamping two clear fused quartz circular disks to a fused quartz cylinder in a metal holder. The cylinder had a side-arm fitted with a ground silica stopper by which it could be filled and emptied without removal from the holder. The disks were 21 mm. in diameter and 1.5 mm. thick. The cylinder was 1.00 cm. long and had an outer diameter of 20 mm. The faces of the disks and the edges of the cylinder were polished optically plane and parallel. The fit was so good that no leakage was perceptible over a period of several hours. The cell holders could be securely mounted in the photometer by means of spring clips.

Considerable difficulty was encountered at the beginning of this investigation because of the fact that the more concentrated sulfuric acid solutions after standing in the cells for about an hour would begin to absorb ultraviolet light very strongly. The trouble was finally traced to the use of crystalline quartz disks. When fused quartz disks were substituted, the sulfuric acid solutions could be kept indefinitely in the cells without any change occurring. The crystalline quartz appeared to be of excellent quality, was very clear, and transmitted ultraviolet light down to the limit of sensitivity of the photographic plate, about 2000 Å., and the source of the difficulty is unknown. A soft glass cylinder also caused similar difficulty.

**Materials.**—The materials were of the highest commercially available purity (C. P. or C. P. analyzed grade).

Sulfuric acid solutions were prepared by dilution of the 95% acid. Analyses of weighed samples by titration with sodium hydroxide agreed to better than two parts per thousand. After standing for over a year in No-Solvit and in flint glass bottles, they were still transparent to ultraviolet light and showed no change in concentration greater than the error of analysis. One hundred per cent. sulfuric acid transparent to ultraviolet light was obtained by distilling sulfur trioxide from 60% fuming acid into the

(8) For a discussion see Gibson, McNicholas, Tyndall, Frehafer and Mathewson, *Scientific Papers of the Bureau of Standards*, No. 440, **18**, 121 (1922).

95% acid in an all-glass apparatus. Benzoic acid and acid potassium phthalate were standard samples from the Bureau of Standards. 2,4-Dinitrophenol was twice crystallized from water after treatment with norite (m. p. 111°). Aniline sulfate was twice crystallized from approximately 1 *N* sulfuric acid after treatment with norite. *p*-Nitrobenzoic acid was twice crystallized from alcohol with one norite treatment, dissolved in 95% sulfuric acid and reprecipitated with ice, then slowly sublimed (m. p. 242°). After each step in the purification the absorption spectrum in 0.1 *M* hydrochloric acid was determined. It remained unchanged throughout the process. Phenylacetic acid was recrystallized from water several times (m. p. 77°). The acidimetric titers of these acids and of the aniline sulfate were found to be correct within two parts per thousand. Anthraquinone was crystallized from glacial acetic acid after treatment with norite; dissolved in 95% sulfuric acid and reprecipitated with ice, then crystallized again from acetic acid. Another sample was crystallized from benzene, then from alcohol, precipitated from 95% sulfuric acid, again crystallized from alcohol and finally crystallized from glacial acetic acid. Both products had identical absorption spectra in 95% sulfuric acid, and the spectrum of the second sample was not changed by the last crystallization.

The late Professor J. L. R. Morgan generously provided a sample of acetophenone which had been very carefully purified in the work of Morgan and Lammert,<sup>9</sup> and which had been kept in a paraffin sealed bottle in a dark closet since 1924. During this time its melting point had dropped from 19.65 to 18.9°. It contained a small amount of absorbing impurity because the spectrum in 95% sulfuric acid of the liquid residue remaining after some 98% had been slowly frozen out differed from that of the original sample. It was purified by twenty-five fractional freezings. These were carried out by slowly freezing (over a period of eight hours) all but 1 cc. of an originally 100-cc. sample, pouring off the liquid, and discarding it. The sample was preserved and the operations were carried out in the exclusion of daylight. The final sample had a melting point of 19.65 ± 0.02°, further fractional freezing had no effect on the melting point, and the spectrum of a small unfrozen residue was identical with that of the whole sample. The sample was carefully protected from moisture and light and its freezing point remained unchanged over a period of about a month.

#### Method

An approximately 0.002 *M* solution of the substance whose absorption spectrum was to be determined was made up by weighing out the calculated amount of solute and adding 50 cc. of solvent. Absorption spectra of this solution and of successive two or three fold dilutions of it were taken until the complete character of the absorption was brought out. This required from three to six plates. In the case of phenylacetic acid and aniline, a more concentrated original solution had to be made up because of the weak absorption of these substances. In all cases the plates were taken on the same day that the solutions were made up and usually within four hours. All measurements were made at room temperature, about 22 ± 5°.

(9) Morgan and Lammert, *THIS JOURNAL*, **46**, 881 (1924).

The plates, which were the Eastman 33 type, were developed with a contrast developer, fixed with Eastman Acid Fixer, washed and dried. They were then mounted over an opal glass in an illuminated stand and match points were visually determined and recorded. The sector setting then gave immediately the value of the logarithm of the transmission *T*, and from this the extinction coefficient *k* for this wave length was obtained by Beer's law

$$k = -\log T/cl \quad (1)$$

where *c* is concentration in moles per liter and *l* is the length (in this case 1.00 cm.) in centimeters of the path traversed by the light through the solution. The extinction coefficients were then plotted against wave length on semi-logarithmic paper. Since at least twenty points were obtained from each plate, each absorption spectrum thus contained at least sixty points, in a fairly even logarithmic distribution. (See curve 8 in Fig. 4 where the experimental points are plotted.)

Inasmuch as some errors were likely to be introduced in the manipulative details of preparing the solutions in addition to the instrumental error of the apparatus itself, the error in the extinction coefficients is probably about 5%, and more often than not is less than this.

If Beer's law holds, the absorption spectrum from one solution should overlap and run smoothly into the absorption spectrum of its next dilution. This was always found to be the case within the experimental error. In those cases where dilution might change the amount of ionization and thereby result in failure of Beer's law, a buffer solution was used as the solvent in order to prevent this.

The calculation of acid or base strength was made as follows. If a solute exists in two forms, say B and BH<sup>+</sup>, so that the total concentration *c* is equal to the sum of the concentrations of these two forms

$$c = c_B + c_{BH^+} \quad (2)$$

and if, as seems generally to be the case, each substance absorbs independently of the presence of the other, then<sup>7</sup>

$$-\log T = (k_B c_B + k_{BH^+} c_{BH^+})l \quad (3)$$

and it follows from equations (1), (2) and (3) that

$$(c_{BH^+}/c_B) = (k - k_B)/(k_{BH^+} - k) \quad (4)$$

In a dilute aqueous solution, *k<sub>B</sub>* may be determined by reducing the acidity to the point where the concentration of BH<sup>+</sup> is vanishingly small; *k<sub>BH<sup>+</sup></sub>* similarly by increasing the acidity. Knowing these, a measurement of *k* in some solution of intermediate acidity permits the calculation of *c<sub>BH<sup>+</sup></sub>*/*c<sub>B</sub>* and from this, if the pH of the solution is known, of the ionization constant of the base. The modifications of the above considerations necessary if the ionization constant of a weak acid HA which ionizes to H<sup>+</sup> and A<sup>-</sup> is to be measured are obvious. In the measurement of the strengths of very weak bases in strong sulfuric acid solutions, certain complications, which will be discussed later, arise from the fact that the change of acidity involves necessarily a significant change in the nature of the medium with a concomitant change in the absorption spectrum.

#### Measurements in Dilute Aqueous Solution

**The Acid Strength of Benzoic Acid.**—The absorption of benzoic acid was determined in the

following solvents: (1) 0.1 *N* sulfuric acid; (2) a buffer containing 0.10 *M* sodium acetate and 0.35 *M* acetic acid (this solvent is transparent in most of the range of wave lengths available);

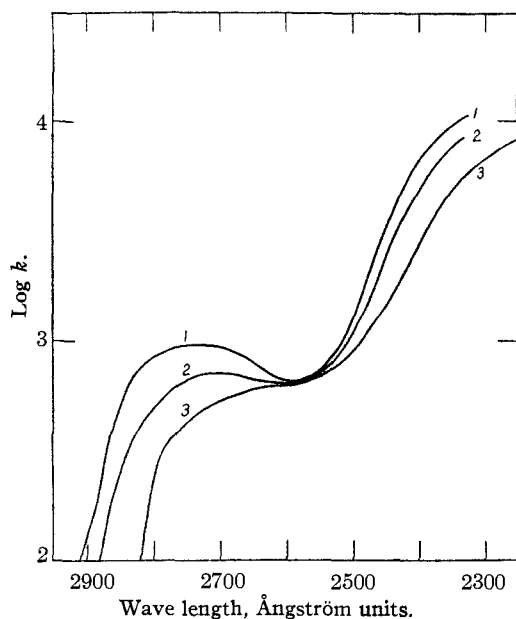


Fig. 1.—Ionization of benzoic acid as an acid: Curve 1, 0.1 *N* H<sub>2</sub>SO<sub>4</sub>; Curve 2, buffer; Curve 3, 0.1 *N* NaOH.

(3) 0.1 *M* sodium hydroxide. The results are plotted in Fig. 1, and the extinction coefficients are given in Table I.

Wave length, Å.	Extinction coefficients in			<i>pK</i>
	0.1 <i>N</i> H <sub>2</sub> SO <sub>4</sub>	0.1 <i>M</i> NaOH	Buffer	
2857	450	50	225	4.11
2791	840	300	540	4.13
2727	950	475	680	4.10
2667	820	575	680	4.09
2609	675	620	640	..
2553	740	700	720	..
2500	1350	900	1050	3.92
2449	3050	1400	2350	4.35
2400	6450	2300	4500	4.27
2353	9200	4800	7200	4.30

Average 4.16 ± 0.11

The logarithmic ionization constant *pK* was calculated by the equation

$$pK_{HB} = pK_{HA} + \log c_{A^-}/c_{HA} - \log (k - k_{HB})/(k_B - k) \quad (5)$$

derived from substitution of equation (4) in the equation

$$pK_{HB} = pK_{HA} + \log c_{A^-}/c_{HA} - \log c_{B^-}/c_{HB} \quad (6)$$

which is an obvious combination and transformation of the equilibrium expressions for the ioniza-

tion of acetic and benzoic acids. The subscript A refers to acetate and the subscript B to benzoate. For the calculations values of *k*<sub>HB</sub> were taken from curve 1, those of *k*<sub>B<sup>-</sup></sub> from curve 3, and those of *k* from curve 2. The value of *pK*<sub>HA</sub> was taken as 4.76.<sup>10</sup> This equation assumes that the quantity *f*<sub>A<sup>-</sup></sub>*f*<sub>HB</sub>/*f*<sub>HA</sub>*f*<sub>B<sup>-</sup></sub> is unchanged by a transfer from infinite dilution to an ionic strength of 0.1. Within the precision of this assumption, therefore, the *pK*<sub>HB</sub> obtained is the value in terms of activities referred to infinite dilution in water as the standard state

$$pK_{HB} = -\log a_{H^+}a_{B^-}/a_{HB} \quad (7)$$

Table I gives the values of *pK* thus obtained at various wave lengths, omitting those in the neighborhood of the isobestic point, the point where all three curves meet.<sup>11</sup> The average value of 4.16 thus obtained is in satisfactory agreement with the value of 4.20 found in the recent measurements by the conductivity method of Brockman and Kilpatrick<sup>12</sup> and of Saxton and Meier.<sup>13</sup>

The conclusion of Stenström and co-workers<sup>6</sup> that ultraviolet colorimetry cannot be applied to the measurement of the ionization of benzoic acid was apparently due to the limitations of their measurements. They did not determine the complete absorption spectra of benzoic acid but instead measured the wave lengths at which benzoic acid has an extinction coefficient of 800 (*log k* = 2.9). They thereby determined three points of the curve for benzoate ion and three for molecular benzoic acid. Four of these six points happen to fall on the isobestic point where of course no change takes place. The other two points are not in agreement with our measurements.

#### The Acid Strength of 2,4-Dinitrophenol.—

The absorption spectra were determined in the

(10) (a) Harned and Ehlers, *THIS JOURNAL*, **55**, 652 (1933); (b) MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

(11) The existence or non-existence of an isobestic point is a matter of considerable significance in studies of this sort. Suppose a given solute exists in two forms or reaction products (such as a base B and a cation BH<sup>+</sup>) each of which possesses a characteristic absorption which is constant for a series of solutions. If both of the forms have equal extinction coefficients at some wave length, if that is, the absorption curves of the two pure individuals intersect, then all of the solutions must likewise have the same coefficient at this wave length, because they contain only various mixtures of these individuals. The absorption curves of all the solutions, therefore, will pass through this intersection. Conversely, if two absorption curves intersect at a point which is not common to all the other curves, then it must be true either that more than two forms or reaction products of the solute must be present, or else that the change in conditions, for instance, in acidity, which produces the variation in proportion of the two forms also changes their specific absorption by what we have called a medium effect. See Clark, "The Determination of Hydrogen Ions," Baltimore, Md., 1928, pp. 153-154.

(12) Brockman and Kilpatrick, *THIS JOURNAL*, **56**, 1483 (1934).

(13) Saxton and Meier, *ibid.*, **56**, 1919 (1934).

following solvents: (1) 0.1 M sodium hydroxide; (2) a buffer containing 0.55 M acetic acid and

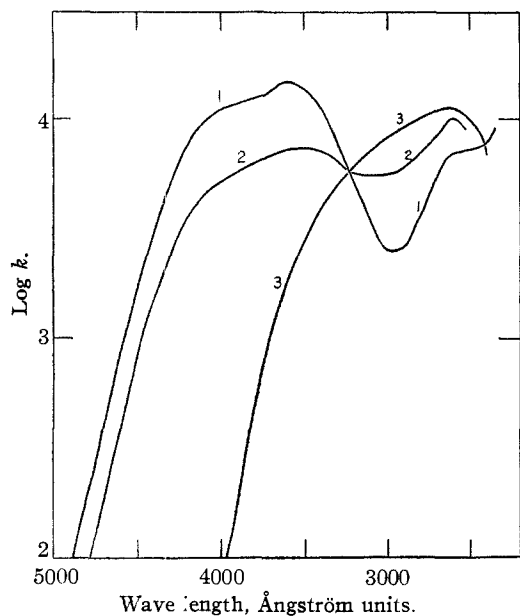


Fig. 2.—Ionization of 2,4-dinitrophenol as an acid: Curve 1, 0.1 N NaOH; Curve 2, buffer; Curve 3, 0.1 N HCl.

0.10 M sodium acetate; (3) 0.1 M hydrochloric acid. The results are shown in Fig. 2 and Table II. In this case the absorption of the anion ex-

TABLE II

Wave length, Å.	2,4-DINITROPHENOL Extinction coefficients in			pK
	0.1 M HCl	0.1 M NaOH	Buffer	
4615	0	750	300	4.20
4444	0	2500	1100	4.12
4286	0	5800	2500	4.14
4138	0	8800	3950	4.11
4000	0	10800	4900	4.10
3871	250	11700	5500	4.09
3750	630	12500	6500	4.03
3636	1,600	14500	7300	4.12
3529	2,450	14000	8000	4.05
3429	3,600	11800	7700	4.02
3333	4,800	9000	6800	4.06
3243	5,700	6500	6100	4.02
3158	6,700	4450	5700	4.12
3077	7,400	3250	5400	4.05
3000	8,000	2500	5500	4.10
2927	8,500	2400	5700	4.09
2857	9,000	3050	6300	4.10
2791	9,600	3800	7100	4.14
2727	10,200	4650	7900	4.17
2667	11,000	6000	8900	4.16
2609	11,200	6900	10000	4.43 <sup>a</sup>
2553	10,900	7200	9100	4.04
Average				4.10

<sup>a</sup> Omitted from average.

= 0.04

tends well into the visible, and this part of the spectrum as well as the ultraviolet is included. The average value of  $pK = 4.10$  agrees excellently with the value of 4.09 obtained by von Halban and Kortum<sup>14</sup> and with the earlier conductivity results quoted in the Landolt-Börnstein "Tabellen."

**The Base Strength of Aniline.**—The absorption spectra of aniline were determined in the

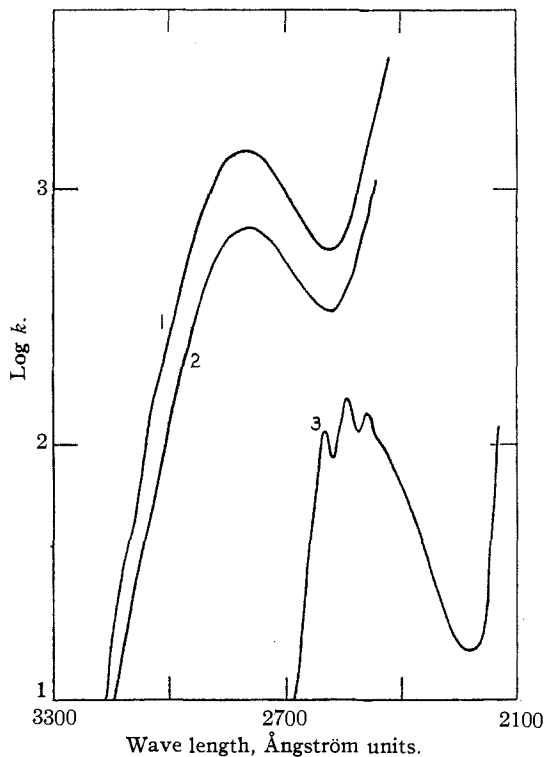


Fig. 3.—Ionization of aniline as a base: Curve 1, 0.1 M NaOH; Curve 2, buffer; Curve 3, 0.1 M H<sub>2</sub>SO<sub>4</sub>.

following solvents: (1) 0.1 M sodium hydroxide; (2) a buffer solution containing 0.080 M acetic

TABLE III

Wave length, Å.	ANILINE Extinction coefficients in			pK'
	0.1 M H <sub>2</sub> SO <sub>4</sub>	0.1 M NaOH	Buffer	
3077	0	63	36	4.51
3000	0	275	130	4.68
2927	0	710	340	4.67
2857	0	1300	620	4.67
2791	0	1480	710	4.67
2727	0	1200	600	4.63
2667	14	810	440	4.57
2609	88	590	345	4.61
2553	120	630	375	4.63
2500	113	1250	630	4.71
Average				4.64 ± 0.05

(14) Von Halban and Kortum, *Z. Elektrochem.*, **40**, 502 (1934).

acid and 0.10 *M* sodium acetate; (3) 0.1 *M* sulfuric acid. For convenience the solutions were prepared from anilinium sulfate rather than from aniline. The results are shown in Fig. 3 and Table III.

In computing the base strength from these curves, it is not possible to correct for salt effects as simply as in the case of the acids because the activity coefficient terms do not cancel out. The base strength of aniline is defined by

$$\begin{aligned} pK'_A &= -\log a_{H^+}a_A/a_{AH^+} \\ &= pH - \log f_A/f_{AH^+} - \log c_A/c_{AH^+} \\ &= pH - \log f_A/f_{AH^+} - \log (k - k_{AH^+})/(k_A - k) \end{aligned} \quad (8)$$

The *pH* of the buffer was calculated from the tables of A. A. Green<sup>15</sup> and found to be 4.75. The activity coefficient term was computed from the formula based on the Debye-Hückel theory.  $-\log f_A/f_{AH^+} = +\log f_{AH^+} = 0.5 \sqrt{\mu}/(1 + \sqrt{\mu})$  (10) This gives a value of  $\log f_{AH^+} = -0.12$ , for the ionic strength of 0.1 which prevailed.

The average value of  $pK'$  obtained is in excellent agreement with the value of 4.66 given in the Landolt-Börnstein "Tabellen" and based upon hydrolysis measurements by both conductivity and indicator methods.

#### Some Cases of Small Change in Absorption.—

It should not be concluded that spectrophotometry in the quartz ultraviolet is a perfectly general method for the determination of ionization. Thus the change in ultraviolet absorption when phenylacetic acid ionizes to phenylacetate ion is appreciable<sup>16</sup> but too small to permit a useful estimate of acid strength. Similarly, the conversion of *p*-nitrobenzoic acid to *p*-nitrobenzoate ion also results in only a small change in this part of the ultraviolet absorption (see Fig. 8). However, our results, together with data in the literature, tend toward the conclusion that with the majority of organic substances ionization results in a change in ultraviolet absorption above 2000 Å. and that ultraviolet spectrophotometry in the range accessible to an ordinary quartz spectrograph is a very general method for measuring ionization.

#### The Strengths of Some Very Weak Bases

**Acetophenone.**—Acetophenone has been shown to behave as a monobasic strong electrolyte when it is dissolved in pure sulfuric acid.<sup>3a</sup> The substance is therefore capable of undergoing the reaction



For such a weak base, the work of Hammett and Deyrup<sup>5</sup> carried out by the methods of visual colorimetry lead one to expect the following changes in light absorption with varying concentration of sulfuric acid-water mixtures. Within a relatively narrow range of concentrations there will be a large change in absorption accompanying the ionization represented by equation I. Outside this range there will be a smaller change in absorption due not to a chemical reaction but to the gradual variation in the nature of the medium in which the substance  $C_6H_5COCH_3$  or the substance  $C_6H_5COH^+CH_3$  is dissolved. The absorption spectra of acetophenone shown in Fig. 4 and Table IV agree entirely with this prediction. There is only a small change in absorption, consisting essentially in a shift toward longer wave lengths in the range from 0 to 55% sulfuric acid (Curves 1 and 2). The same thing is true in the region above 86% sulfuric acid (Curves 8 and 9). In the intermediate region (Curves 2 to 8) there is a much more rapid change which is no longer of the nature of a lateral shift. It is rather of a sort which can hardly be attributed to any other cause than the presence in the solution in varying amounts of two substances, one of which has an absorption much like curve 2, the other one similar to curve 8. The composite nature of the intermediate curves is particularly apparent in curves 4 and 5.

The qualitative picture, that ionization according to equation I takes place in the region from 55 to 86% sulfuric acid, while only a medium effect—a slow lateral shift in the absorption curves—occurs at higher and lower concentrations, seems very well established. The quantitative treatment is more difficult because the same medium effect must be expected to exist also in the region of ionization. That it is present is demonstrated by the failure to obtain a true isobestic point.<sup>11</sup>

In order to calculate the base strength we use the values (taken from large scale plots) of the acidity function  $H_0$  which have been obtained in previous work.<sup>5</sup> This acidity function has been shown<sup>5</sup> to be uniquely determined in these solutions by the equation

$$H_0 = pK'_B - \log c_{BH^+}/c_B \quad (11)$$

where B is any base and

$$pK'_B \equiv -\log \frac{a_{H^+}a_B}{a_{BH^+}} \quad (12)$$

(15) A. A. Green, *THIS JOURNAL*, **55**, 2331 (1933).

(16) Ley and Hünecke, *Ber.*, **59**, 521 (1926).

TABLE IV  
 EXTINCTION COEFFICIENTS OF ACETOPHENONE IN H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O MIXTURES

Wave length, Å.	% H <sub>2</sub> SO <sub>4</sub>									
	0.0	50.03	55.0	65.15	70.45	73.65	77.66	80.40	85.96	95.99
3700	0	0	0	0	0	0	0	120	175	300
3600	0	0	0	0	0	130	240	360	530	850
3500	0	0	0	60	175	325	580	840	1120	1500
3400	0	0	0	110	370	650	1100	1400	1750	2100
3300	0	0	0	200	670	960	1480	1820	2080	2400
3200	55	90	95	380	890	1300	1850	2250	2600	2900
3100	105	220	300	770	1550	2200	3200	4100	5400	7200
3000	310	680	840	1800	3700	5800	9400	12300	15400	20500
2900	900	1350	1590	3400	6600	10000	13900	17200	19900	20500
2800	1150	1800	2260	4750	7800	10500	12700	13300	13700	12000
2700	1400	3000	3800	6500	8400	9000	8700	8200	6500	4600
2600	4300	7700	8400	10000	9000	7700	5800	4200	2600	1500
2500	11000	11500	11700	10100	7500	5800	3350	2000	900	400
2400	11000	9000	8600	6200	4300	3000	1650	830	375	200
2300	5700	4100	3800	2400	1800	1200	680	500	420	380

is the measure of the strength of the base in terms of activities. By combination of equations (11) and (4) we obtain

$$pK'_B = H_0 - \log(k - k_{BH^+}) / (k_B - k) \quad (13)$$

which is of course closely analogous to equation (9). Because of the medium effect, however, pure non-ionized acetophenone must have a different absorption in say 70% sulfuric acid from that which it possesses in water or even in 50% acid. We cannot, therefore, use the extinction coefficient of acetophenone in water solution as the value of  $k_B$ , nor can we use the coefficient in 100% sulfuric acid as the value of  $k_{BH^+}$ , even though we know that it is practically non-ionized in the former solvent and practically all ionized in the latter.

We have used two methods of correcting for this medium effect error, both dependent upon the assumption that the medium effect consists essentially in a lateral shift of the spectrum within the range of ionization as it does without this range. The first method was evolved from the following considerations. Suppose that in the neighborhood of some wave length at which the  $pK'$  is to be calculated, the reference curve for ionized acetophenone is very steep while the reference curve for non-ionized acetophenone is more or less flat. Now if the medium effect is causing the curves to shift, the reference curve for ionized acetophenone will be in great error because of its steepness, whereas the extinction coefficients of the curve for non-ionized acetophenone will be only slightly affected because of the flatness of the curve in the neighborhood of the wave length under consideration. Thus in

calculating the  $pK'$  by means of formula (13), the error will be due primarily to the large error in  $k_{BH^+}$  resulting from the medium effect. There will, therefore, be considerable advantage if the  $pK'$  is calculated from experimental values of  $k$  and  $k_B$  alone in this range of wave lengths. There will be a similar advantage in using only  $k$  and  $k_{BH^+}$  in a range of wave lengths where the curve for ionized acetophenone is flat and that for the non-ionized compound is steep.

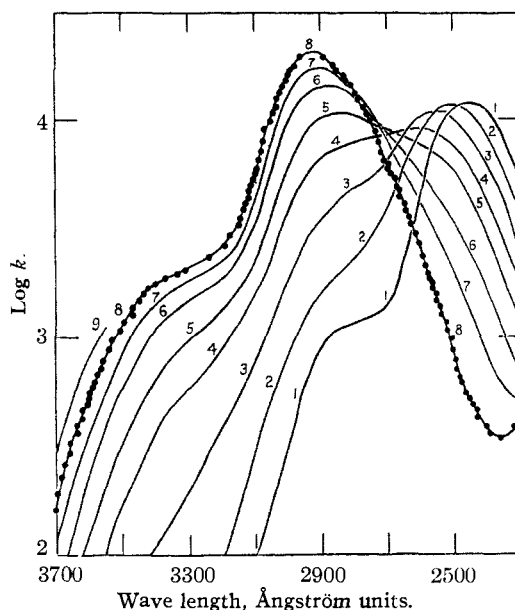


Fig. 4.—Ionization of acetophenone as a base: Curve 1, solvent is water; other curves sulfuric acid—2, 55%; 3, 65.15%; 4, 70.45%; 5, 73.65%; 6, 77.66%; 7, 80.40%; 8, 85.96%; 9, 95.99%.

For purposes of this calculation we transform equation (13) to the form

$\text{antilog}(-pK_b) \equiv K =$

$$\text{antilog}(-H_0) \times (k - k_{\text{BH}^+}) / (k_{\text{B}} - k)$$

or

$$K = h_0 (k - k_{\text{BH}^+}) / (k_{\text{B}} - k) \quad (14)$$

where

$$h_0 \equiv \text{antilog}(-H_0) \quad (15)$$

Formula (14) may be put into two forms

$$K + k_{\text{BH}^+} [h_0 / (k_{\text{B}} - k)] - h_0 k / (k_{\text{B}} - k) = 0 \quad (16)$$

$$1/K + k_{\text{B}} [1/h_0 (k_{\text{BH}^+} - k)] - k/h_0 (k_{\text{BH}^+} - k) = 0 \quad (17)$$

Both of these equations are of the form

$$a + bx - y = 0 \quad (18)$$

where  $x$  and  $y$  are known quantities and  $a$  and  $b$  may be calculated, if two sets of values for  $x$  and  $y$  are known. If more than two sets of values of  $x$  and  $y$  are known, it is of course best to use a least squares solution. Formula (16) is to be used when the reference curve for non-ionized acetophenone is the flatter and formula (17) at those wave lengths at which the curve for ionized acetophenone is flatter. At those wave lengths where both curves are equally flat, formula (13) should give satisfactory values.

The reference curves for the ionized and for the non-ionized substance should obviously be taken as near the range of ionization as possible, yet sufficiently removed so that the substance is present essentially in one form, ionized or non-ionized only. To make this choice we have used the following procedure: a rough value of  $pK'$  was calculated using reference curves well outside the region of ionization. Using this approximate value, a calculation was made of the range of sulfuric acid concentration in which ionization of acetophenone would be less than 5% and greater than 95%. An appropriate safety factor was then allowed to take care of the error in the  $pK'$ . In this way, 55% sulfuric acid was chosen as the reference solvent for non-ionized acetophenone, and 86% sulfuric acid as the reference solvent for completely ionized acetophenone.

In deciding which reference curve is the flatter, the plot of  $\log k$  against the wave length is misleading because of its logarithmic nature. Accordingly, the curves were replotted using  $k$  instead of  $\log k$  as ordinate. Inspection of these curves revealed which reference curve and, therefore, which equation should be used for each wave length. The equations so chosen are listed in Table V which contains the results of the calculation.

The second method of calculation depends upon the principle that all of the absorption

TABLE V  
- $pK'$  VALUES OF ACETOPHENONE COMPUTED BY LEAST SQUARES

Wave length, Å.	Equation	% H <sub>2</sub> SO <sub>4</sub>					Average	Deviation
		65.15	70.45	73.65	77.66	80.40		
3500	16	6.10	6.27	6.32	6.34	6.17	6.25	0.08
3400	16	6.04	6.13	6.18	6.16	6.10	6.13	.04
3300	13	5.87	5.92	6.07	6.09	6.03	6.00	.08
3200	13	5.79	5.93	6.03	6.11	6.09	5.99	.10
3100	16	5.80	5.97	6.08	6.12	5.88	5.99	.10
3000	16	6.01	6.16	6.23	6.23	6.09	6.15	.08
2900	13	5.86	6.03	6.07	6.17	6.12	6.05	.08
2800	16?	5.46	5.64	5.61	5.52	5.57	5.56 <sup>a</sup>	.06
2700	..	..	..	..	..	..	..	..
2600	17?	6.31	6.30	6.30	6.33	6.30	6.31 <sup>a</sup>	.01
2500	17	6.00	5.89	5.98	5.99	5.97	5.96	.03
2400	17	5.80	5.77	5.82	5.86	5.73	5.79	.04
2300	17	5.58	5.74	5.69	5.57	5.42	5.58 <sup>a</sup>	.09
							Average 6.03 ±	0.10

<sup>a</sup> Omitted from final average.

curves due to mixtures in varying proportions of two substances (in this case the base and the cation) must intersect in a single point if any two intersect and if there is no medium effect.<sup>11</sup> If the medium effect represents a shift in wave length only, without change in shape or height of the bands, it should be possible to compensate for its effect by shifting all of the absorption curves laterally to produce a single intersection, an isobestic point, somewhere in the middle of the ionization region. Inspection of the curves of Fig. 4 shows that Curves 4 and 5 are very close to what would be expected for approximately 50% ionization. We have, therefore, shifted the curves for other solvents laterally so that they all pass through the intersection of these two

TABLE VI  
- $pK'$  VALUES FOR ACETOPHENONE BY ISOBESTIC POINT METHOD

Wave length, Å.	% H <sub>2</sub> SO <sub>4</sub>					Average	Deviation
	65.15	70.45	73.65	77.66	80.40		
3600	..	..	6.05	6.32	5.98	6.12	0.14
3500	..	6.07	6.05	6.18	6.06	6.09	.04
3400	5.87	6.01	6.02	6.13	5.91	5.99	.08
3300	5.94	6.02	6.03	6.10	5.93	6.00	.06
3200	5.74	5.89	5.92	6.01	5.79	5.87	.08
3100	5.67 <sup>a</sup>	4.86 <sup>a</sup>	5.65 <sup>a</sup>	5.82 <sup>a</sup>	..	5.50 <sup>a</sup>	.32
3000	5.69 <sup>a</sup>	5.85 <sup>a</sup>	5.66 <sup>a</sup>	5.63 <sup>a</sup>	..	5.71 <sup>a</sup>	.07
2900	5.83	6.02	6.03	6.15	6.04	6.01	.08
2800	5.77	5.96	6.04	6.12	6.22	6.02	.13
2700	..	5.89	6.06	6.23	..	6.06	.11
2600	..	6.06	6.00	6.06	5.78	5.98	.10
2500	5.85	5.99	5.99	6.04	5.80	5.93	.09
2400	..	6.32	6.08	6.21	6.08	6.17	.09
Average	5.83	6.02	6.03	6.14	5.96	6.02	
Deviation	0.05	0.08	0.03	0.07	0.12	0.08	

<sup>a</sup> Omitted from average.



curves and have then calculated the  $pK'$  of acetophenone from these shifted curves. The results are given in Table VI.

The average values of  $pK'$  obtained by the two methods agree excellently. Furthermore, both methods show only a random variation of  $pK'$  with wave length. (This is most decidedly not the case if no account is taken of the medium effect.) All in all, it seems probable that this quantity, which has never before been measured in even the most approximate fashion, is now known within at least 0.1 unit.

A solution of acetophenone in 0.1 *M* aqueous hydrochloric acid would therefore be converted to the cation  $C_6H_5COH^+CH_3$  to the extent of only one part in ten million. This is of course a figure of interest for the interpretation of such acid-catalyzed reactions of acetophenone as the bromination. The base acetophenone is nearly  $10^{10}$  weaker than aniline; compared with nitrogen bases it is intermediate in strength between 2,4-dinitroaniline and 6-bromo-2,4-dinitroaniline, but is still over a thousand times stronger than 2,4,6-trinitroaniline; compared with other oxygen bases, its strength lies between that of  $\beta$ -benzoylnaphthalene and that of *p*-benzoyldiphenyl, and it is only about 0.4 logarithmic unit weaker than the familiar "halochromic" ketone benzalacetophenone.

**Some Considerations about Indicators.**—A medium effect was recognized in the colorimetric work in sulfuric acid–water mixtures of Hammett and Deyrup<sup>5a</sup> where it appeared as a variation in color intensity. There was no visible change in color quality which would have rendered a colorimetric match impossible. Yet the lateral shifts of the whole absorption curve toward longer wave lengths to which we now apply the same term, might, at first sight, be expected to result much more in a change in color quality than one in intensity. The explanation of the apparent contradiction derives from certain properties of human vision combined with the fact that the indicators studied were all of the colorless–yellow type. Their colorimetric behavior depends, therefore, upon the absorption by the yellow form of frequencies in the violet. In this range the human eye has little if any sense of color quality and it apprehends a shift in the absorption curve simply as a change in intensity without a concomitant change in color quality.<sup>17</sup> Thus the

(17) Gibson and Tyndall, *Bureau of Standards Scientific Paper* No. 475 (1923).

medium effect does not interfere with obtaining a colorimetric match, and all that need be corrected for is the change in intensity, which is not too difficult.

If, however, the indicator changed from colorless to let us say, blue, an evaluation of the medium effect would be very difficult because a small shift in the absorption spectrum due to the medium effect would not only change the intensity of the absorbed light but also its color, and it would be impossible to obtain a match in the colorimeter. This result has some application to colorimetric measurements in dilute aqueous solution, where medium effects due to changes in ionic strength or other variations in composition are larger than is sometimes appreciated. The nitrophenol indicators of Michaelis avoid color matching difficulties in this way, because they change from colorless to strong yellow.

An example of the difficulties which may result from the medium effect may be found in the work of Baker.<sup>18</sup> His work on the basic properties of organic oxygen compounds is of the greatest significance and interest, but he appears to have been misled by a medium effect in respect to the range of acidity in which acetophenone ionizes. He considered that the ionization occurs in the region in which the pale yellow color possessed by acetophenone in concentrated sulfuric acid is developing. Now in Fig. 4 the curves have been so drawn that an intercept on the ordinate of 3700 Å. corresponds to a visible yellow color in a solution containing a few thousandths molar acetophenone. It will be seen that the color does not appear until the acetophenone is practically completely converted to the ion and that the deepening of the yellow color with increasing concentration of sulfuric acid is due solely to the shift resulting from the medium effect. The change in absorption due to ionization occurs entirely in the ultraviolet.

**Benzoic Acid.**—This substance is also known to be a strong monoacid base in 100% sulfuric acid.<sup>3</sup> The absorption spectra were determined in sulfuric acid–water mixtures from 0.5 to 100% sulfuric acid. Some of the curves are given in Fig. 5. Only a medium effect shift to higher wave lengths appears between 0.5 and 70.20% sulfuric acid (Curves 1 and 2) and the large change corresponding to the basic ionization occurs between 70.20 and 95.65% sulfuric acid (Curves 3 to 5,

(18) Baker, *J. Chem. Soc.*, 307 (1931).

TABLE VII  
EXTINCTION COEFFICIENTS OF BENZOIC ACID IN H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O MIXTURES  
Extinction coefficients for 0.5% = 0.1 N H<sub>2</sub>SO<sub>4</sub> are in Table I

Wave length, Å.	70.20	76.11	77.66	80.40	81.84	83.46	85.69	90.52	95.65	100.0
3243	0	0	25	50	75	85	120	220	310	360
3158	0	60	100	185	260	340	500	790	970	1130
3077	15	170	250	450	600	790	1025	1440	1600	1800
3000	120	360	470	750	960	1150	1450	1840	1950	2040
2927	390	710	800	1120	1270	1420	1625	1920	1950	1900
2857	910	1125	1180	1340	1450	1600	1665	1890	1930	1950
2791	1150	1330	1360	1500	1580	1780	1900	2500	2760	2840
2727	1130	1500	1600	2100	2550	3200	4100	6100	7880	8560
2667	1060	2060	2700	4080	5500	6800	8800	12350	14050	15600
2609	1400	3200	4100	6320	8150	9700	12100	15350	16050	17700
2553	2550	5000	6050	8250	9850	11000	12160	14750	14800	14350
2500	5100	7700	8500	9650	10650	11400	11200	12350	11600	10400
2449	8450	10300	10450	10000	10300	10750	9500	8850	7800	7000
2400	10700	10900	10800	9650	9200	8800	7500	5900	4750	4150
2353	11000	10500	9750	8200	7600	6800	5480	3900	2720	2130
2308	9700	8650	7800	6500	5800	4850	3600	2440	1660	1180
2264	7450	6400	5500	4400	3800	3080	2200	1350	870	560
2222	5600	4200	3800	2850	2300	2000	1300	800	455	300
2182	3450	2600	2400	1750	1520	1250	880	615	405	320

inclusive). Above 95.65% sulfuric acid there is again a shift corresponding to the medium effect. Curves 3 and 4 for the solvents 81.84 and 83.46% sulfuric acid correspond approximately to half ionization. The extinction coefficients for the various solvents are given in Table VII.

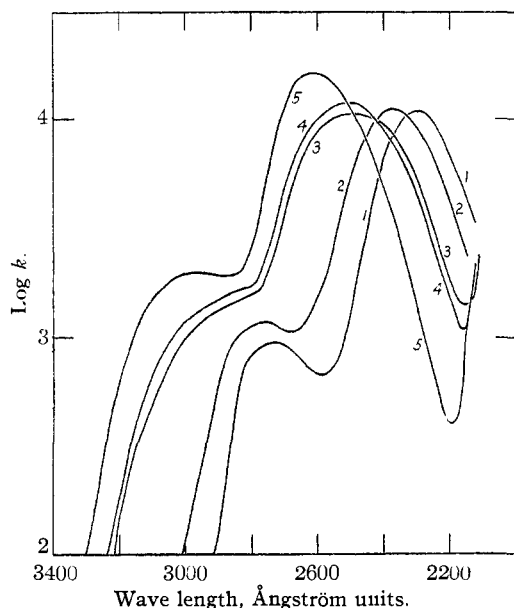


Fig. 5.—Ionization of benzoic acid as a base in sulfuric acid: Curve 1, 0.5% (0.1 N); 2, 70.20%; 3, 81.84%; 4, 83.46%; 5, 95.65%.

The  $pK'$  values computed by the least squares method (or by equation (13) where both refer-

ence curves are flat) are contained in Table VIII. The concentration of ion was assumed to be negligible in 70.20% acid, and the ionization was taken as essentially complete in 95.65% acid. Values were also computed by the second method, shifting the curves laterally so that they all passed through the intersection of Curves 3 and 4 at a wave length of 2430 Å. and an extinction coefficient of 10,000. This gave a value of  $-7.11 \pm 0.10$  from the data on 83.46% acid and  $-7.09 \pm 0.04$  from those on 81.84% acid. These are in fair agreement with the average of  $-7.26$  ob-

TABLE VIII  
 $-pK'$  VALUES OF BENZOIC ACID COMPUTED BY LEAST SQUARES

Wave length, Å.	Equation	Average $-pK'$ for seven solvents	Deviation
3243	16	7.56	0.12
3158	16	7.51	.08
3077	16	7.33	.08
3000	13	7.17	.08
2927	17	7.01	.15
2857	17	7.11	.07
2791	16	7.31	.22
2727	16	7.59	.07
2667	16	7.40	.06
2609	13	7.16	.09
2353	17	7.33	.10
2308	17	7.22	.07
2264	17	7.11	.08
2222	17	7.09	.07
2182	17	7.07	.06

Average,  $7.26 \pm 0.16$

tained by the least squares method, which should be considered the more reliable.

The base benzoic acid is from 1 to 1.5 logarithmic units weaker than the various phenyl ketones previously studied. The wide spread between the first and second acidity constants of the cation  $C_6H_5C(OH)_2^+$  is worthy of note but not unexpected in view of the small distance between the two hydrogens. The acidity of a solution in which benzoic acid is half ionized to benzoate ion must be increased about 11.5 logarithmic units in order to convert it to a half ionized base.

**Anthraquinone.**—The base strength has previously been determined by the colorimetric method.<sup>5a,b</sup> Absorption curves are given in Fig. 6 and extinction coefficients in Table IX. The solubility in aqueous sulfuric acid of less than 85% concentration is so small that the determination of a reference absorption spectrum for the non-ionized base is impracticable. The  $pK'$  values must, therefore, be calculated from equation (17), which can be applied without serious error only in regions where the curve for  $BH^+$  is flat. This limits us in this case to the region around 4000 Å. From the absorption at 100 Å intervals between 4400 and 3900 we obtain an average  $pK'$  of  $-8.18 \pm 0.19$ , which agrees well with the value of  $-8.15$  from visual colorimetry.

TABLE IX

EXTINCTION COEFFICIENTS OF ANTHRAQUINONE IN  $H_2SO_4 + H_2O$  MIXTURES

Wave length, Å.	% $H_2SO_4$					
	85.96	89.27	90.52	92.97	95.99	100.0
4500	1080	1750	1900	2300	3000	4250
4400	1700	3100	3500	4300	5200	6400
4300	2600	4700	5300	6200	7400	8300
4200	3550	5400	6000	7500	8800	9500
4100	4150	5750	6300	8200	9400	9900
4000	4800	5950	6500	8100	9300	9700
3900	5300	6000	6550	7300	8600	8800
3800	5600	6000	6300	6500	7300	7500
3700	5600	5800	5900	5800	6000	5600
3600	5200	5000	4800	4500	4400	3900
3500	4500	3850	3750	3100	2800	2600
3400	3600	2750	2500	2150	1800	1750
3300	2500	1900	1700	1600	1300	1300
3200	2800	2900	3000	3200	4000	4400
3100	6600	9200	9900	11200	12500	12700
3000	7500	8800	9000	9300	9800	9400
2900	10500	8200	7600	6500	5550	5400
2800	9500	7000	6700	6400	5800	5600
2700	23000	29000	35000	35000	39000	39000
2600	45000	37000	35000	32000	29000	26000
2500	21000	18000	17000	16000	15000	14000

The low precision is due, at least in part, to the low dispersion of the spectrograph used in this range of wave lengths.

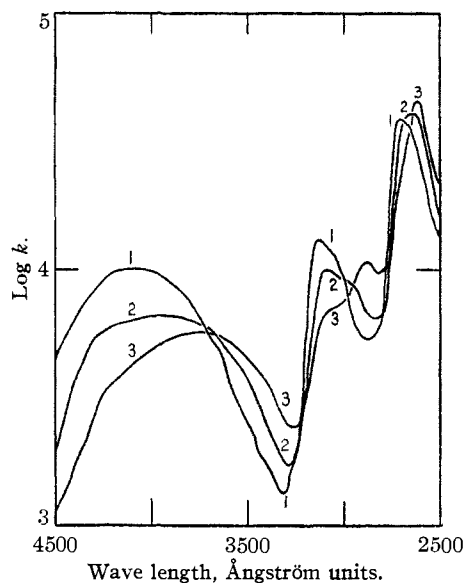


Fig. 6.—Ionization of anthraquinone as a base in sulfuric acid as solvent: Curve 1, 100.0%; 2, 90.52%; 3, 85.96%.

**Phenylacetic Acid.**—In spite of the fact that there is very little change in absorption when phenylacetic acid ionizes to phenylacetate ion,<sup>16</sup> there is a fairly large change when this acid gains rather than loses a hydrogen ion. Results of absorption measurements are shown in Fig. 7 and Table X.

TABLE X

EXTINCTION COEFFICIENTS OF PHENYLACETIC ACID IN  $H_2SO_4 + H_2O$  MIXTURES

Wave length, Å.	% $H_2SO_4$				
	70.20	76.11	81.84	85.69	90.52
2800	0	0	10	26	68
2750	0	0	26	65	160
2700	22	30	69	130	260
2650	90	95	150	240	400
2600	138	142	225	350	500
2550	165	183	260	400	600
2500	140	178	290	460	700
2450	117	168	330	550	840
2400	126	205	405	640	950
2350	200	320	560	770	1130
2300	405	520	770	1000	1290
2250	720	850	1050	1270	1550
2200	1300	1430	1650	1600	1840

Above 90% sulfuric acid, the absorption changes rapidly with time, probably as a result of sulfonation. Thus the spectrum of a solution in 95.99% acid taken within an hour after prepa-

ration was similar in shape to curve 3 in Fig. 7 but displaced upward. The spectrum after three hours is shown in Curve 4. At 90% sulfuric acid or less the rate of this change is negligible. It is, therefore, impracticable to determine the absorption of the completely ionized form, and the  $pK'$  must be calculated from measurements on the non-ionized base and on partially ionized mixtures, using equation (16). The average value obtained from wave lengths of 2350, 2400, 2450, 2500 and 2550 Å., in the region in which the curve for the non-ionized base is flat, is  $-7.59 \pm 0.13$ .

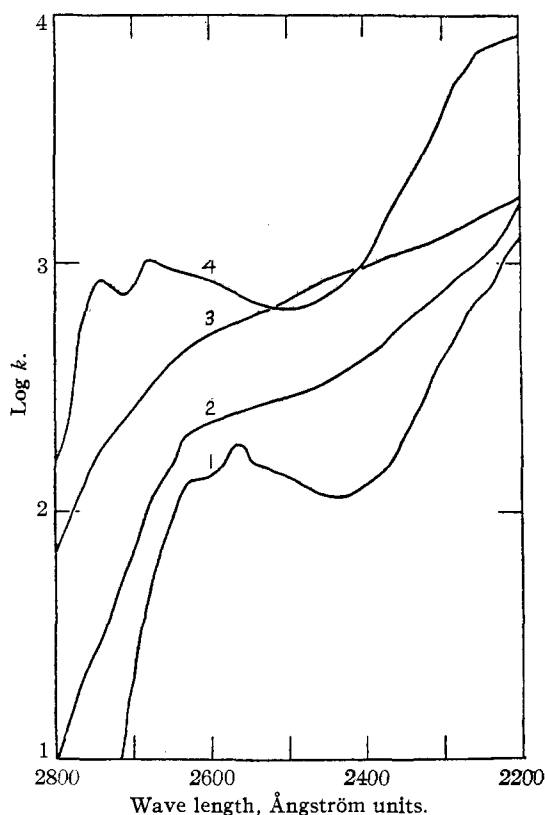


Fig. 7.—Ionization of phenylacetic acid as a base in sulfuric acid: Curve 1, 70.20%; 2, 81.84%; 3, 90.52%; 4, 95.99% (stood three hours).

It will be noted that base strength does not go inversely as acid strength. Phenylacetic acid is both a slightly weaker acid and a slightly weaker base than benzoic acid.

Although the base strengths of benzoic and phenylacetic acids are very nearly the same, the reaction rates of their acid catalyzed esterifications are very different.<sup>19</sup> Thus the esterification of phenylacetic acid with absolute ethyl

(19) Goldschmidt, *Ber.*, **28**, 3218 (1895).

alcohol in the presence of catalyzing hydrochloric acid is almost a hundred times faster than the corresponding esterification of benzoic acid.

It has not infrequently been implied in discussions of the acid catalysis of esterification that the rate should be uniquely determined by the base strength of the acid being esterified. This is evidently not the case.

***p*-Nitrobenzoic Acid.**—We have already pointed out that the change in ultraviolet absorption attending the ionization of this substance into *p*-nitrobenzoate ion is too small to permit measurement of the acid strength by this method (see Fig. 8). The ionization as a base also takes place with very little change in ultraviolet absorption. (It is completely ionized in 100% sulfuric acid.<sup>3</sup>) In fact the whole change in absorption from 0.1 *M* sodium hydroxide to 95.65% sulfuric acid might reasonably be attributed to medium effect alone. There is no obvious reason why this should be the case.

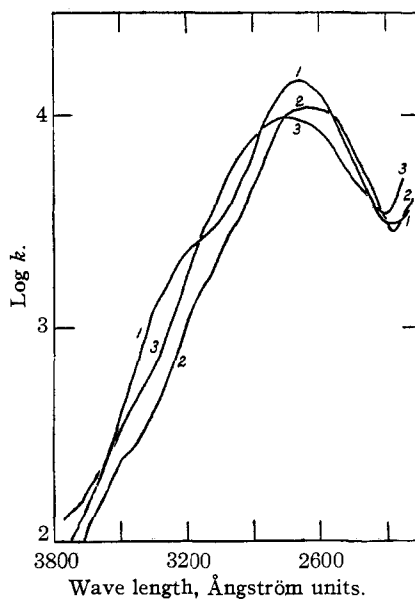


Fig. 8.—*p*-Nitrobenzoic acid: Curve 1, 95.65%  $H_2SO_4$ ; Curve 2, 0.1 *M* HCl; Curve 3, 0.1 *M* NaOH.

We wish to acknowledge the kindness of Professors H. T. Beans and H. C. Urey, who made available for us apparatus which was indispensable for this work.

### Summary

1. The ultraviolet absorption spectra in various solvents have been determined of benzoic acid, 2,4-dinitrophenol, aniline, acetophenone,

anthraquinone, phenylacetic acid and *p*-nitrobenzoic acid.

2. The validity of ultraviolet spectrophotometry as a method of measuring ionization has been demonstrated for a carboxylic acid and a phenol, and for an oxygen and a nitrogen base.

3. Mathematical methods have been devised for taking into account the effect of changing

solvent in measuring the strength of very weak bases.

4. Criteria have been established for the choice of indicators to be used in changing media.

5. The strengths of the following very weak bases have been measured: acetophenone, benzoic acid and phenylacetic acid.

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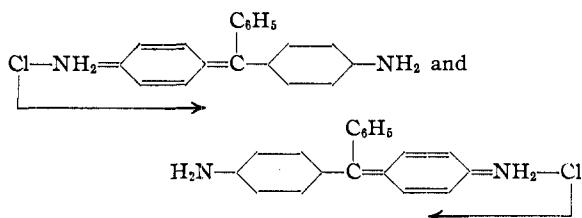
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[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES]

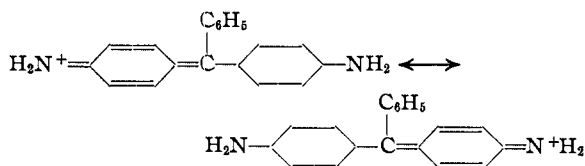
## Auxochromes and Resonance

BY C. R. BURY

Baeyer<sup>1</sup> suggested that the color of the triphenylmethane dyes was due to the oscillation of an atom in the molecule. Döbner's violet (the hydrochloride of *p,p*-diaminotriphenylcarbinol) was considered to be in a state of oscillation between the two forms



Now that the distinction between electrovalent and covalent bonds is known, it is clear that the oscillation is purely structural



since change from one form to the other involves movement of electrons only, but no movement of atoms. Further, such an oscillation is to be expected: it is merely an example of resonance. Baeyer's hypothesis can be restated in terms of modern theory as follows. The intense absorption of light that characterizes dyes is due to an intimate association of a chromophore and of resonance in the molecule.

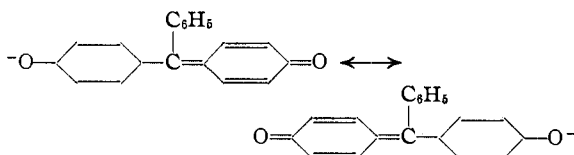
There is much indirect evidence that this hypothesis is true, not only for the triphenylmethane dyes, but also for most of the best investigated types of dyes. In particular, it gives some explanation of the function of an auxochrome.

(1) Baeyer, *Ann.*, **354**, 152 (1907).

Willstätter and Piccard<sup>2</sup> called attention to the fact that certain simple compounds containing the quinonoid group were colorless, or very feebly colored: the development of color in these compounds depends on the introduction of certain substituent groups—auxochromes. In the light of the hypothesis put forward, the function of the auxochrome is to introduce the possibility of resonance. (Auxochromes also facilitate the attachment of the dye to the fabric, but this aspect is not considered further here.)

The hypothesis enables one to understand what groups can act as chromophores and what positions they must occupy. Thus, fuchsonimine  $\text{HN}=\text{C}_6\text{H}_4=\text{C}-(\text{C}_6\text{H}_5)_2$  is colorless, though it contains the same chromophore as Döbner's violet. Introduction of an amino group in the *p*-position results in the development of color and the possibility of resonance. Other substituent groups are ineffective in producing color, though they may alter the shade of color of a dye that already contains an amino group. The amino group may be alkylated ( $-\text{NR}_2$ ), but conversion to a trialkyl substituted group ( $-\text{N}^+\text{R}_3$ ) renders resonance impossible and is found in practice to render it ineffective. The destruction of the color of methyl violet and similar dyes by excess concentrated acid can be attributed to the same change.

The color of the hydroxytriphenylmethane dyes is associated with a similar resonance, *e. g.*, the anion of benzaurin.



(2) Willstätter and Piccard, *Ber.*, **41**, 1458 (1908).