after twenty minutes, washed with nitric acid of pH 1, and dried in the usual manner. The pH of the filtrate was 1.10. In two experiments, 63.4 and 63.5 mg., respectively, of copper was found. The precipitates of copper quinaldate were examined spectrographically for zinc, and faint lines at 3345, 3072 and 3035 Å. were observed. No attempt was made to estimate the amount of zinc present. The filtrate from one determination gave a negative test for copper with hydrogen sulfide. As the results were slightly low, it would appear that no appreciable amount of zinc had been entrained; likewise, no copper remained unprecipitated.

In the above solution, copper should be quantitatively precipitated at pH 0.72 and upward, while zinc begins to precipitate at pH 1.22. A better separation would doubtless have been obtained at a lower pH, even though only enough zinc precipitated to be detected spectroscopically under the conditions used.

(b) **The Separation of Copper from Cadmium.** —Majundar[5] and Shennan[3,4] have disagreed on the feasibility of this separation. Recalculating some data given by Majundar,[5] it appears that with $[Cu^{++}] = 2 \times 10^{-3}$ and $[Cd^{++}] = 2.5 \times 10^{-3}$, and using about 5×10^{-3} molar quinaldic acid, a quantitative separation of the copper was obtained at a pH of about 2. This corresponds closely to the theoretical value, as nearly as it can be estimated using the approximate molar concentrations calculated from the experiments described.

It can be shown that the safe range for separation of equimolar quantities of copper and cadmium is about 0.7 pH unit, with cadmium quinaldate precipitating at the higher value. Thus

the results of Majundar,[5] which are satisfactory from an analytical standpoint, also seem well based theoretically.

Separations involving other ions listed in Table I may be treated analogously. Certain quinaldates, such as silver, mercury (I) and (II), tungsten, and molybdenum, are insoluble at such low pH values that their interference in any determination of copper, zinc, or cadmium would be certain.

3. **Calculation of Fraction Precipitated.**—A third possible application of this type of data is the calculation, for any given concentration of metallic ion, hydrogen ion, and precipitant, of the fraction that will precipitate. If the ratio of quinaldic acid to metallic ion is R, then $R = [H\dot{Q}_0]/[M_0^{++}]$, and α is given by

$$-4\alpha^3 + 4\alpha^2(R+1) - \alpha(4R + R^2) + R^2 = \frac{[H^+]^2 S}{[M_0^{++}]^3 [K_a]^2}$$

The solution of the cubic equation is most readily found by making successive approximations, as the useful root will lie between zero and one.

The authors wish to acknowledge the assistance of Mr. Roman Dreywood in preparing the quinaldic acid, and in conducting qualitative tests on the reactions of quinaldic acid.

Summary

1. The solubility products of some insoluble quinaldates have been determined by a method involving fractional precipitation.

2. Applications of solubility data to problems of precipitation and separation with quinaldic acid are cited.

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The Ultraviolet Absorption Spectra and Resonance in Benzene Derivatives—Sulfanilamide, Metanilamide, p-Aminobenzoic Acid, Benzenesulfonamide, Benzoic Acid and Aniline

BY W. D. KUMLER AND L. A. STRAIT

It is well known that the absorption of light by molecules is associated with the phenomenon of resonance.[1,2,3,4] In this communication are reported measurements of the absorption spectra of some benzene derivatives in acid, basic and water or sodium chloride solutions. An interpretation of the resulting spectra is given in terms of the resonance forms used by organic chemists for

about a decade[5,6,7,8] to account for various other properties of such molecules.

Experimental

The spectrophotometric data were obtained with the aid of a Hilger Spekker photometer and a Hilger medium quartz flat-field spectrograph (E498). The source of ultraviolet light was the continuous spectrum of hydrogen

(1) Bury, THIS JOURNAL, **57**, 2115 (1935).

(2) Lewis and Calvin, Chem. Rev., **25**, 273 (1939).

(3) Sklar, J. Chem. Phys., **5**, 669 (1937).

(4) Pauling, Proc. Natl. Acad. Sci., **25**, 557 (1939).

(5) Ingold, Chem. Rev., **15**, 225 (1934).

(6) Kumler and Porter, THIS JOURNAL, **56**, 2549 (1934).

(7) Sutton, Trans. Faraday Soc., **30**, 789 (1934).

(8) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.

excited in a low voltage d.c. discharge tube made by the Bartol Foundation. The spectrograph slit width, 0.125 mm., was the same for all of the spectrograms. This corresponds to an "effective" slit width of 1 and 2 Å. at the ends of the wave length region 2300 to 3000 Å., respectively. The absorption cells were 2 cm. in length. Eastman Kodak Co. Spectrum Analysis No. 1 photographic plates were used for all of the spectrograms except in those cases where the solvent was sufficiently transparent at wave lengths lower than 2300 Å., where the use of Eastman IOuv sensitized emulsions extended the range of measurements. An A. R. L. densitometer was employed to increase the accuracy of selection of match points.

Materials

Aniline.—J. T. Baker C. P. aniline was distilled from zinc dust. It had a boiling point of 184.6–184.7°.

Benzenesulfonamide.—The material taken was from the same sample used by Kumler and Halverstadt[9] in determining the dipole moment. It had a melting point of 156–157°.

Sulfanilamide.—The compound was from the same sample used by Kumler and Halverstadt.[9] The product melted at 165–166°.

Metanilamide.—This compound was from the same sample used by Kumler and Halverstadt.[9] It melted at 140°.

p-Aminobenzoic Acid.—Eastman Kodak Company best grade was treated twice with charcoal and crystallized two times from alcohol. The product melted at 187°.

**Benzoic Acid.**—Reagent benzoic acid was used. It had a melting point of 122°.

Discussion

Effect of Solvent.—Lewis and Calvin[2] have stated that, contrary to a wide-spread belief, the dielectric constant of the medium does not have a pronounced influence upon optical absorption, except possibly in the case of compounds of the type of p-nitroaniline. Since some of the compounds we are considering are of this type it seemed desirable to see whether their absorption was appreciably altered by the addition of an electrolyte such as sodium chloride. It was found that with the two compounds investigated (p-nitroaniline and sulfanilamide) there was no detectable difference in their absorption curves in water and in 1 N sodium chloride, which indicates that even with compounds of this type the dielectric constant as such has very little effect on the absorption spectrum. The fact that the spectrum of p-nitroaniline is somewhat different in hexane, dioxane and water[2] we attribute not to the difference in the dielectric constants of these solvents but to the difference in solvation due to the different possibilities for hydrogen bond formation in the three cases. That the dielectric constant is not the major factor is further indicated by the relative magnitude of the shift of the main absorption band in the successive solvents. Thus the band shifts more in going from hexane with dielectric constant of 1.8 to dioxane with a dielectric constant of 2.1 than it does in going from dioxane to water with a dielectric constant of 81. On the other hand, with hexane, p-nitroaniline can form no hydrogen bonds; with dioxane, hydrogen bonds can be formed between the amino group

(9) Kumler and Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

and the solvent; while with water, hydrogen bonds can be formed between the solvent and both the amino and nitro groups. It thus appears likely that p-nitroaniline type compounds are not an exception to the generalization of Lewis and Calvin,[2] "that all pronounced changes in color, when passing from one solvent to another, are due to such definite solvates. . . ."

In view of the fact that the dielectric constant of the medium has very small if any effect on the absorption we can be reasonably sure in comparing the absorption of a compound in water or in 1 N sodium chloride solution with its spectrum in 1 N acid or base that the marked alterations of absorption (Figs. 1, 3, 4, 5) result from factors other than the difference in dielectric constant of the medium.

Spectra in Acid.—The striking phenomenon that aniline in acid has only about one-fiftieth of the absorption it has in water had been noted by several workers[10,11,12] and the decreased absorption in the anilinium ion has been associated by some investigators[11,12] with the inability of an electron to migrate from the amino group to the ring. From our viewpoint the effect may be explained as follows: In aniline the absorption of light is determined chiefly by the contributions of the forms $H_2\overset{+}{N}\!=\!\!\langle\overline{}\rangle\!-$, etc. In acid these forms are excluded because the ion $H_3\overset{+}{N}\!-\!\!\langle\rangle$ already has 4 bonds attached to the nitrogen and this is the maximum number possible. Hence, the only resonance present to account for the absorption of light, $H_3\overset{+}{N}\!-\!\!\langle\overset{+-}{}\rangle$ etc., is analogous to that responsible for the absorption of light in benzene[2] or toluene, $\pm\langle\overline{}\rangle\!\mp$, etc. The spectrum of aniline in acid is thus very similar to that of toluene or benzene. Since this amino resonance will thus be blocked when any aromatic amino compound is completely converted to the salt, it follows that the spectrum of any aromatic amino compound will revert in acid to the spectrum of the compound in which the amino group is replaced by hydrogen or an alkyl group. There is considerable evidence in the literature to support this conclusion.[10,13]

Benzenesulfonamide has considerably more absorption than benzene or toluene due to contribu-

(10) Wohl, *Bull. soc. chim.*, **6**, 1312 (1939).

(11) Kato and Someno, *Inst. Phys. Chem. Res.* (Tokyo), **33**, 211 (1937).

(12) Sklar, *J. Chem. Phys.*, **7**, 984 (1939). Two of the absorption curves in Fig. 2 of this article are incorrectly labeled. The curve labeled benzene is actually that of dimethylaniline hydrochloride, see Landolt–Börnstein, "Phys. Chem. Tab.," Egb. III, p. 1377. The curve labeled anilinium ion is the curve for benzene.

(13) Dede and Rosenberg, *Ber.*, **67**, 147 (1934). In Landolt–Börnstein, "Phys. Chem. Tab.," Egb. III, pp. 1353 and 1354, the curves for o-amino benzoic acid and p-aminobenzoic acid taken from the paper by Dede and Rosenberg have apparently been mislabeled. Thus in Landolt–Börnstein the curves for o-aminobenzoic acid are labeled p-Amido-Benzoesäure and the curves for p-aminobenzoic acid are labeled o-Amido-Benzoesäure.

tions of the structures $+$⟨benzene ring⟩$=\overset{\overset{\bar{O}}{\|}}{\underset{\|}{S}}-NH_2$, etc.

If the amino and sulfonamide groups are on the ring in the meta position, as in metanilamide, an interesting situation arises. The amino group cannot resonate with the sulfonamide group in the meta position, but one might expect contributions from forms in which the amino group resonates with the ring $H_2\overset{+}{N}=$⟨benzene ring⟩$-\overset{O}{\underset{O}{S}}-NH_2$, etc., and

from forms in which the sulfonamide group resonates with the ring H_2N-⟨benzene ring⟩$=\overset{O}{\underset{O}{S}}-NH_2$, etc. But

these two resonances are incompatible because in one case a negative charge is placed on the 2, 4 and 6 carbon atoms; in the other case a positive charge is placed on the same carbon atoms. One would then expect the character of the spectrum to be determined almost entirely by the stronger resonance even though it be but slightly greater than the other resonance. Aniline has a greater extinction coefficient than benzenesulfonamide, indicating that the aniline resonance is stronger.
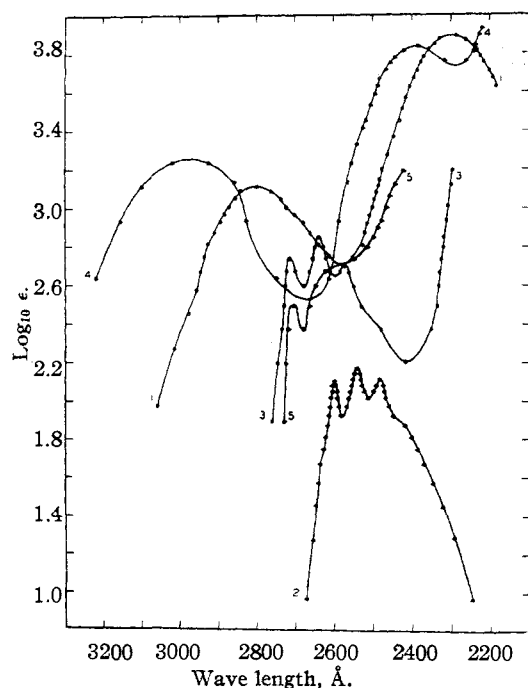

Fig. 1.—1, O, Aniline in water; 2, -o-, aniline in 0.5 N hydrochloric acid; 3, ●, benzenesulfonamide in water; 4, o-, metanilamide in 1 N sodium chloride; 5, ●-, benzenesulfonamide in 0.9 N sodium hydroxide.
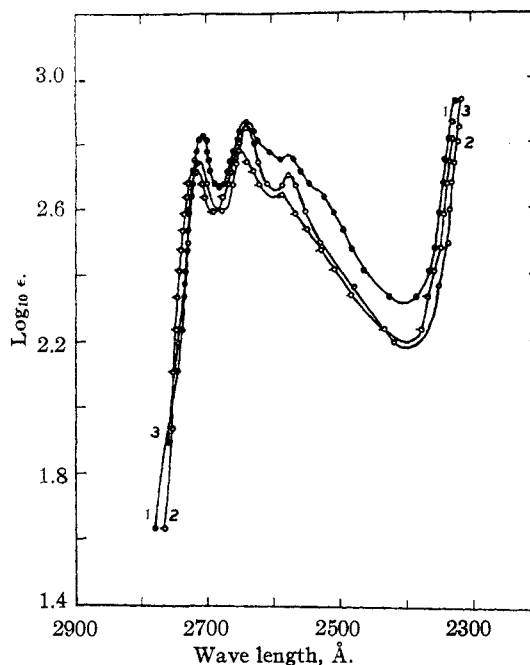

Fig. 2.—1, ●, Sulfanilamide in 0.8 N hydrochloric acid; 2, -o-, metanilamide in 0.8 N hydrochloric acid; 3, O, benzenesulfonamide in water.
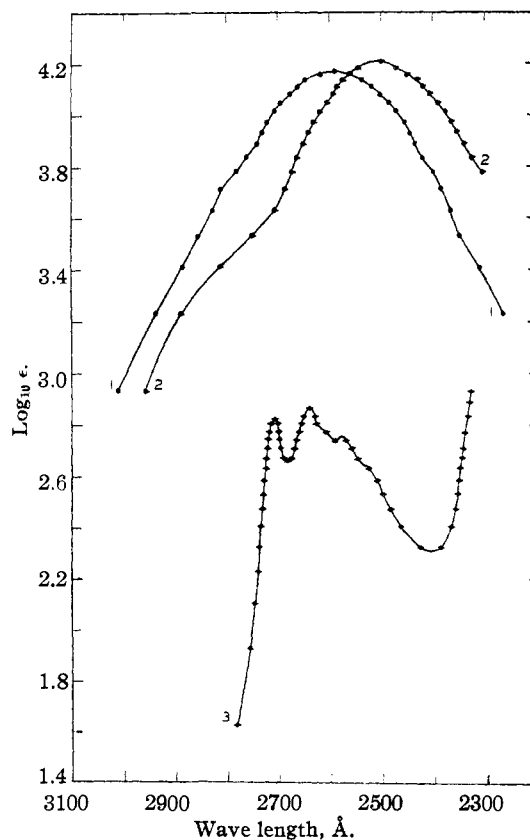

Fig. 3.—1, ●, Sulfanilamide in 1 N sodium chloride; 2, o-, sulfanilamide in 1 N sodium hydroxide; 3, -o-, sulfanilamide in 0.8 N hydrochloric acid.
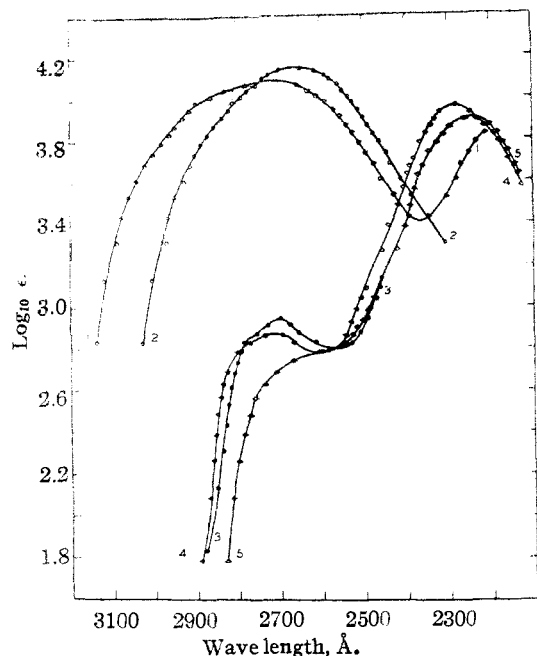
Fig. 4.—1, o-, p-Aminobenzoic acid in 1 N sodium chloride; 2, O, p-aminobenzoic acid in 1 N sodium hydroxide; 3, ●, p-aminobenzoic acid in 1 N hydrochloric acid; 4, o-, benzoic acid in water; 5, -o-, benzoic acid in 0.01 N sodium hydroxide.

Fig. 5.—1, o-, Metanilamide in 1 N sodium chloride; 2, ●, metanilamide in 1 N sodium hydroxide; 3, O, metanilamide in 0.8 N hydrochloric acid.

Hence, the spectrum of metanilamide is very similar to that of aniline and quite different from that of benzenesulfonamide (Fig. 1). The curve of metanilamide in base (Fig. 5) is an even closer approach to that of aniline in water, as might be expected.

In acid solution the aniline resonance in metanilamide is blocked and the spectrum should revert to that of benzenesulfonamide since the presence of acid will not block the sulfonamide resonance. Figure 2 shows the very similar nature of these two spectra.

With sulfanilamide a strong resonance is possible between the amino and the sulfonamide group

with the forms of the type $H_2N=\langle\rangle=S-NH_2$

making the greatest contribution. As a result sulfanilamide has a considerably higher extinction coefficient than either aniline, benzenesulfonamide or metanilamide and, furthermore, the character of the spectrum is quite different from that of these other compounds.

When sulfanilamide is placed in acid solution both the resonance between the amino group and the ring, and that between the amino group and the sulfonamide group, is blocked. Hence, here again the spectrum reverts to that of benzenesulfonamide (Figs. 2 and 3). It is striking that spectra as different as those of metanilamide and sulfanilamide when measured in water or 1 N sodium
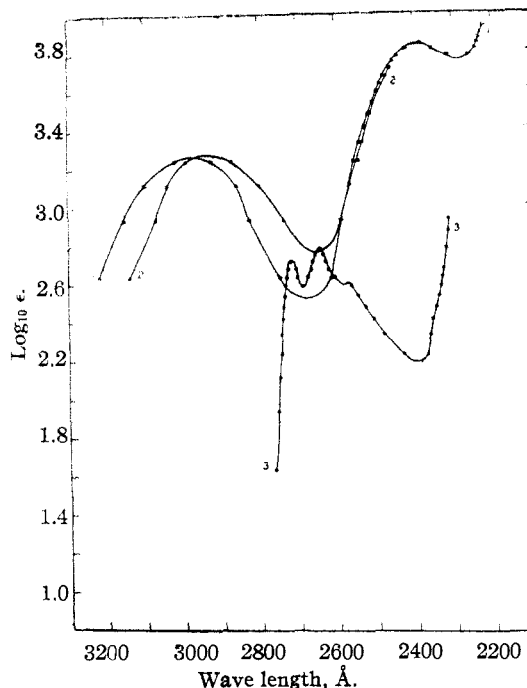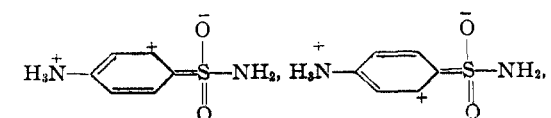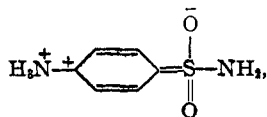
chloride should both become in acid solution virtually identical with the spectra of benzenesulfonamide (Fig. 2). This observation together with the resulting explanation lends weight to the contention that the nature of the spectrum of benzene derivatives may be associated with the contribution of the usual resonating forms employed by the organic chemist. The fact that the three spectra are so nearly alike suggests also that too much emphasis has been placed in the past on the "weighting" effect of groups in accounting for the alteration of spectra. It appears that the weight of the group as such has very little effect on the spectra. The crucial factor seems rather to be whether or not the introduction of a group makes possible new resonating forms or alters those already present.

In solutions such as water or sodium chloride where the resonance between the amino and the sulfonamide group is not blocked, sulfanilamide has about thirty times the absorption it has when this resonance is blocked. The form involved

in this resonance $H_2\overset{+}{N}=\langle\rangle=\overset{O}{\underset{O}{S}}-NH_2$ is much

more stable than the forms involved in the resonance in acid

$H_3\overset{+}{N}-\langle\rangle-\overset{\overset{-}{O}}{\underset{O}{S}}-NH_2, H_3\overset{+}{N}-\langle\rangle-\overset{\overset{-}{O}}{\underset{O}{S}}-NH_2,$

$$H_3\overset{+}{N}\!-\!\!\!\!\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!=\!\!\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\!-\!NH_3,$$

etc.; consequently its absorption is much greater.

The spectrum of *p*-aminobenzoic acid in water or in *N* sodium chloride solution is somewhat similar to that of sulfanilamide. In acid solution the spectrum becomes very similar to the spectrum of benzoic acid, since the amino group in acid cannot resonate with the ring or with the carboxyl group.

Spectra in Basic Solutions.—In going to basic solutions it will be seen in Figs. 1, 3, 4 and 5 that the compounds do not behave in a uniform fashion as they did when placed in acid solution. In some cases the extinction coefficient is increased; in others it is decreased or unchanged. This phenomenon also is explicable in terms of the contributions of the usual resonating forms.

With benzoic acid contributions of the forms

$$+\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!=\!\!\overset{\overset{\bar{O}}{\|}}{C}\!\!\diagdown_{OH}\!\!\!,\ \text{etc., are mainly responsible}$$
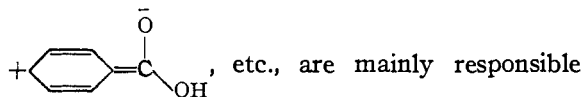
for the light absorption in the near ultraviolet range. This resonance is in competition with the

nance in the carboxyl group $\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!\diagdown_{\overset{+}{O}H}$
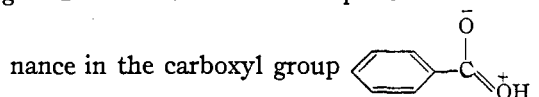
In the ion the carboxyl resonance is much stronger than in the free acid; as a consequence the resonance between the carboxyl group and the ring will suffer. Hence, the extinction coefficient is less in base than in water as is seen in Fig. 4.

In *p*-aminobenzoic acid and sulfanilamide just the opposite is observed. In basic solution the extinction coefficient is greater than in water solution (Fig. 4). Since the same effect that caused the extinction coefficient of benzoic acid to be less in base than in water must also be functioning in these compounds, the fact that with the latter compounds the coefficient is greater in base means that a new factor of fairly large magnitude is involved. The nature of this factor to our knowledge has not been discussed and we wish to suggest the following hypothesis. The presence of a charge in one part of a body or a molecule will, of course, induce dipoles in other parts thus − + − with the opposite pole of the dipole nearer the inducing charge. However, if there is a preferred path in a molecule whereby a ± arrangement can be set up without violating the ordinary valences of the atoms, then the presence of a charge may augment this ± structure even though the dipole is not in the position it would occupy if the charge induced a dipole in an isotropic body. It is such an effect that we believe responsible for the observation that these compounds have a greater extinction coefficient in base than in water. *p*-Aminobenzoic acid has a preferred path in which a separation of charge

can be set up with all atoms having ordinary valences $H_2\overset{+}{N}\!\!=\!\!\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!=\!\!\overset{\overset{O}{\|}}{C}\!\!\diagdown_{OH}$, consequently when a negative charge is placed on the carboxyl group the charge augments the contribution of

the form $H_2\overset{+}{N}\!\!=\!\!\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!=\!\!\overset{\overset{\bar{O}}{\|}}{C}\!\!\diagdown_{O}$ so this form makes

a greater contribution in the ion than it does in the free acid. With benzoic acid the corresponding form involves unusual valences with three

bonded carbon atoms $+\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!=\!\!\overset{\overset{\bar{O}}{\|}}{C}\!\!\diagdown_{O}$ and here

the effect is very small and not of sufficient magnitude to overcome the reduction in this form resulting from the greater carboxyl resonance in the ion.[14]

That sulfanilamide has a higher extinction coefficient in base than in water is likewise evidence for a greater contribution from the form with separation of charge in the ion, compared with the undissociated molecule. In another paper this fact is significant in correlating structure and bacteriostatic activity of the sulfonamides.[14a]

Benzenesulfonamide like benzoic acid has a lower extinction coefficient in base than in water. This may be explained by the fact that in this compound there is likewise no preferred path with usual valences for the electrons to take in establishing a form with a separation of charge. In base what appears to be a new band (Fig. 1) with a high extinction coefficient is present at about 2400 Å. This may be interpreted as follows. In the ion the charge has a marked tendency to go to the oxygen atoms resulting in a

large contribution from the forms $\underset{}{\langle\!\!\!=\!\!\!\rangle}\!\!-\!\!\overset{\overset{\bar{O}}{\|}}{\underset{\underset{O}{\|}}{S}}\!\!=\!\!NH,$

(14) That the augmenting effect of the negative charge may take place in several steps in the case of sulfanilamide has been suggested to us by Professor M. Calvin. The presence of the negative charge induces a positive charge on the sulfur. The electrons from the N⁴ nitrogen are drawn into the ring by this plus charge and the quinoidal structure results with effective neutralization of the plus charge on the sulfur and increase of the plus charge on the N⁴ nitrogen.

Another factor to be considered is the fact that although *p*-aminobenzoic acid is a fairly weak acid, $Ka = 2.1 \times 10^{-5}$, there will be an appreciable proportion of the ion present at the concentrations used in these measurements. Curve 1, Fig. 4, may be then a composite curve for the acid plus an appreciable amount of its ion. If the wave lengths of the absorption maxima for the two species are separated far enough the resultant observed curve could have a lower extinction coefficient at maximum than the curve for the ion even though the extinction coefficient of the acid were actually greater than that for the ion. It appears doubtful that these curves are widely enough separated for such an interpretation. Furthermore, this explanation would not account for the observed higher extinction coefficient of the ion in the case of sulfanilamide for here there is less than 0.1% of the ion present when the compound is dissolved in water or sodium chloride solution.

(14a) Kumler and Daniels, THIS JOURNAL, **65**, 2190 (1943).

etc., with a double bond between sulfur and nitrogen. This bond must be a very strong chromophor[2] and the new band in the ion is tentatively attributed to it. The above resonance will diminish the contributions from the resonance form

+〈＝〉＝S—NH, etc., responsible for the other
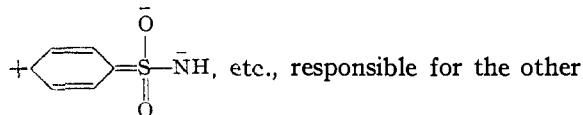
bands in the spectrum so they will have lower extinction coefficients in base, as is observed.

Previously it was seen that the spectrum of metanilamide was determined largely by the amino resonance. Since only the sulfonamide resonance is appreciably altered in going to basic solution, such a change makes but little difference in the extinction coefficient of metanilamide. In Fig. 5 it is seen that the long wave length band has very nearly the same extinction coefficient in base as in sodium chloride and the short wave length band as far as it has been obtained in basic solution corresponds to the analogous band in sodium chloride solution.

It is to be noted that the long wave length bands in all cases shift to shorter wave length in going to basic solutions. This is true regardless of whether the extinction coefficient increases or decreases when the solvent is made basic. This increase in vibrational frequency may be considered a reflection of the effective increase of the force constant of the electronic oscillator due to the presence of the added ionic charge.

Our absorption curve for aniline in acid shows more structure than some reported in the literature,[11,15] but agrees with a more recent measurement.[16] The lack of structure reported may be due either to insufficient resolving power or more likely, as in at least one instance, the acid concentration was not high enough to convert sufficient of the aniline to the salt. The shape of the absorption curve for aniline in acid is very similar to those for benzenesulfonamide, sulfanilamide in acid and metanilamide in acid, although the extinction coefficient is only about one-fifth that of the other compounds. Each curve has three main peaks with about 60 Å. separation. A fourth lower peak at shorter wave length is evident in three of the curves and the aniline curve shows an inflection on the long wave length side indicating a fifth band. The fine structure here probably arises from vibrational transitions although there appears to be a qualitative correlation between the number of possible resonating forms and the extinction coefficients of the various bands.

(15) Scheibe, Ber., 59, 2617 (1926).
(16) Flexser, Hammett and Dingwall, THIS JOURNAL, 57, 2103 (1935).

Summary

1.   The ultraviolet absorption curves of sulfanilamide, metanilamide, p-aminobenzoic acid, benzenesulfonamide, benzoic acid and aniline have been determined in acidic, basic and water or sodium chloride solutions.

2.   The spectra of these compounds are correlated with the usual resonating forms employed by the organic chemist.

3.   The spectra of metanilamide in acid and sulfanilamide in acid are very similar to the spectrum of benzenesulfonamide in water. A general rule is developed that the spectrum of any aromatic amino (unsubstituted or alkyl substituted) compound will revert in acid (strong enough to convert it to the salt) to the spectrum of the corresponding compound in which the amino group is replaced by hydrogen or an alkyl group. In the salt the amino group cannot resonate with the ring or any group on the ring so the only resonance for the absorption of light will be that between the other groups and the ring or that within the ring itself.

4.   Sulfanilamide and p-aminobenzoic acid have a higher extinction coefficient in basic than in sodium chloride or water solution. This indicates that the main resonance form makes a greater contribution in the ion than in the undissociated molecule. The reverse is the case with benzoic acid and benzenesulfonamide. An hypothesis is presented which accounts for this effect.

5.   Evidence is presented that compounds of the type of p-nitroaniline are not exceptions to the generalization of Lewis and Calvin that alterations of spectra in different solvents are due to solvation effects and not to a difference in dielectric constants.

6.   The difference in the spectra of p-nitroaniline in hexane, dioxane and water is attributed to the fact that the compound can form no hydrogen bonds with hexane whereas with dioxane it can form hydrogen bonds between the amino group and the solvent, and with water it can form hydrogen bonds between both the amino and nitro groups and the solvent.

7.   The spectrum of metanilamide is similar to the spectrum of aniline and quite different from that of benzenesulfonamide. This is also explained in terms of resonance: The amino and sulfonamide resonances are incompatible (one puts negative, the other positive, charges on the same carbon atoms) and the stronger amino resonance almost entirely determines the character of the metanilamide absorption spectrum.