amine) in quantitative yield. The hydrochloride consisted of colorless needles melting at 248°. The picrate had a melting point of 243°.[10]

Summary

1. It is suggested that the hydrolysis of alkylureas and urethans, when acid or alkali hydrolysis is impracticable, be accomplished by means of phthalic anhydride and subsequently with hydrazine hydrate.

2. This procedure has been utilized in the synthesis of tryptamine.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DYE LABORATORY OF THE CHEMISTRY DIVISION OF THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

THE RELATION BETWEEN THE ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF CERTAIN AZO DYES. I. THE EFFECT OF POSITION ISOMERISM ON THE ABSORPTION SPECTRA OF METHYL DERIVATIVES OF BENZENE-AZOPHENOL[1,2]

BY WALLACE R. BRODE

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The effect of position isomerism on the absorption spectra of similarly constituted aromatic compounds has been studied by Baly,[3] Purvis,[4] Klingstedt[5] and Henri[6] together with their co-workers in this field. In general it has been shown that substitution in the para position produces a stronger absorption band than substitution of the same group in either the ortho or meta position in the benzene ring. This effect, although not always mentioned, can be noted in the data of other observers. Recent work by Henri on the absorption spectra of isomeric xylenes and dihalogenated benzene compounds in the vapor phase has shown considerable variation in the fine structure of the absorption bands with a change in the position of substitution. The unstable nature of azo dyes, however, does not permit the study of their absorption spectra in a vapor state, so that data by this method are unobtainable on the compounds studied in this paper.

The object of this investigation is a fundamental quantitative study

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[10] Ewins, *J. Chem. Soc.*, **99**, 270 (1911).

[1] Publication approved by the Director of the National Bureau of Standards, Department of Commerce.

[2] Presented in part at the Philadelphia meeting of the American Chemical Society in September, 1926.

[3] Baly, *J. Chem. Soc.*, **107**, 1058 (1915).

[4] Purvis, *ibid.*, **103**, 1088 (1913).

[5] Klingstedt, *Compt. rend.*, **175**, 365 (1922).

[6] Henri, "Structure des Molécules," Herman, Paris, **1925**, and unpublished data communicated to the author.

of the relation between the absorption spectra and chemical constitution of simple derivatives of benzene-azophenol. The isomeric series of dyes selected for this study include, together with the parent substance, benzene-azophenol, all the possible mono- and dimethyl derivatives of benzene-azophenol in which not more than one methyl group occurs in a benzene ring. These dyes, prepared from C.P. intermediates, were recrystallized several times from alcohol and analyzed according to the Kolthoff[7] modification of the Knecht and Hibbert[8] titanous chloride titration method for azo dyes (see Table I).

Experimental

The data presented in this paper deal only with these dyes dissolved in a 3% aqueous solution of sodium hydroxide.[9] The alkaline dye solutions for spectrophotometric examination were prepared as follows.

The weighed amount of dye, 0.7200 g. of benzene-azophenol or 0.8450 g. of its various mono- and dimethyl derivatives, was dissolved in 500 ml. of alcohol (95%) at 20°. Fifty ml. of this solution were diluted to 250 ml. with alcohol and then 10 ml. of this latter solution and 10 ml. of a 30% solution of C.P. stick sodium hydroxide in distilled water were diluted to 100 ml. with distilled water. Thus the solutions which were measured contained 2.880 cg. per liter of benzene-azophenol or 3.380 cg. per liter of the mono- and dimethyl derivatives. It should be noted that the solutions as used contained a small amount of alcohol.

The experimental observations were made with a Hilger sector photometer and spectrograph.[10] This apparatus and the system of nomenclature used in the presentation of the data are described in previous papers published in THIS JOURNAL and elsewhere.[11] The data presented are plotted with $-\log_{10}$ transmittancy (intensity of absorption) as the ordinates and frequency in vibrations per 10^{-12} second as the abscissas. In Figs. 1 and 2 the concentrations are the same only when the molecular weights of the compounds are the same. In Table I, however, the absorption values have been corrected for analysis and weight so that all of the indicated values are for the same molecular concentration, that is, 1.5×10^{-4} g. mole per liter. The cell thickness used in all cases was 0.5 cm.

Discussion of Data

An examination of the absorption curves, Figs. 1 and 2, will show that all of these compounds exhibit the same general type of absorption.

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[7] Kolthoff, *Rec. trav. chim.*, **45**, 169 (1926).

[8] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, New York, **1925**.

[9] The absorption spectra of these dyes have also been measured in 95% ethyl alcohol and in concentrated (35%) hydrochloric acid as solvents. For data in these solvents and a more extended presentation of the effects of the sodium hydroxide solvent see a forthcoming paper in the *Bureau of Standards Journal of Research*.

[10] Placed at the author's disposal by the Colorimetry Section of the Bureau of Standards.

[11] (a) Gibson and others, *J. Opt. Soc. Am.*, **10**, 169 (1925); (b) Gibson and others, *Bureau of Standards Sci. Papers* 440, **18**, 121–184 (1922); (c) Brode with Adams, THIS JOURNAL, **46**, 2033 (1924); (d) Brode, *J. Phys. Chem.*, **30**, 56 (1926); (e) Brode, THIS JOURNAL, **48**, 1984 (1926).

TABLE IA

THE INTENSITIES OF THE ABSORPTION BANDS OF THE COMPOUNDS STUDIED IN A 3% AQUEOUS SOLUTION OF SODIUM HYDROXIDE

(Values given in $-\log_{10}$ transmittancy.) Concentration, 1.5×10^{-4} gram mole per liter; cell thickness, 0.5 cm.

Compound		Anal. by $TiCl_3$, %	M. p., °C. (obs.)	M. p., °C. (lit.)[b]	Cg. per liter of pure dye $\equiv$ to 1.5×10^{-4} mole per liter
Benzene-azophenol	(Ph)[a]	99.6	152	152	2.971
Benzene-azo-*o*-cresol	(*o*)	99.2	128	128–130	3.182
Benzene-azo-*m*-cresol	(*m*)	98.5	107	109	3.182
o-Toluene-azophenol	(*o'*)	99.5	102	102–3	3.182
m-Toluene-azophenol	(*m'*)	98.3	140	144–5	3.182
p-Toluene-azophenol	(*p'*)	100.8	151	151	3.182
o-Toluene-azo-*o*-cresol	(*o'-o*)	99.6	132	132	3.392
o-Toluene-azo-*m*-cresol	(*o'-m*)	100.5	113	111	3.392
m-Toluene-azo-*o*-cresol	(*m'-o*)	98.0	114	115	3.392
m-Toluene-azo-*m*-cresol	(*m'-m*)	99.5	106	106–7	3.392
p-Toluene-azo-*o*-cresol	(*p'-o*)	100.2	162	163	3.392
p-Toluene-azo-*m*-cresol	(*p'-m*)	99.7	135	135	3.392

[a] These abbreviations are used in Figs. 1 and 2 as well as other parts of this paper to designate these compounds.

[b] Beilstein, "Handbuch der organischen Chemie," Vol. IV, Ergänzungsband (1906).

TABLE IB

THE MAGNITUDE OF THE ABSORPTION BANDS OF THE COMPOUNDS STUDIED IN A 3% AQUEOUS SOLUTION OF SODIUM HYDROXIDE

Absorption bands		I				II
A (obs.)	*B* (obs.)	*A'* (anal.)	*B'* (anal.)	*A'* + *B'*	*A'*/*A'* + *B'*	
1.70	1.56	1.53	1.29	2.82	0.543	0.60
1.84	1.38	1.82	0.85	2.67	.682	.68
1.55	1.67	1.38	1.29	2.67	.518	.65
1.48	1.63	1.18	1.40	2.58	.457	.61
1.69	1.55	1.50	1.26	2.76	.543	.66
1.77	1.60	1.57	1.32	2.89	.542	.66
(1.63)[a]	(1.51)[a]	1.47	1.06	2.53	.581	.65
1.14	1.63	1.06	1.34	2.40	.442	.61
1.96	1.50	1.92	0.90	2.82	.680	.71
1.53	1.71	1.40	1.31	2.71	.517	.61
2.05	1.26	2.05	1.02	3.07	.668	.72
1.64	1.86	1.52	1.42	2.94	.517	.73

[a] Approximate values.

There is a strong band between 670 and 750 f. and a weaker one between 1125 and 1200 f. The principal band is slightly asymmetric in form, the lower frequency side having a steeper slope than the higher frequency side. Further it is markedly deformed in the region of maximum absorption. Apparently it is composed of two overlapping bands. These components appear to be in equilibrium with each other, for where one of them is increased the other is diminished in intensity (see Table I). This suggests the presence of two slightly different modifications of the compounds in the solutions studied, the proportions of which are influenced by the position of the substituting group.

From a study of the absorption bands of these and similar compounds in various other solvents,[9,11d,11e] it may be seen that in any one solvent,

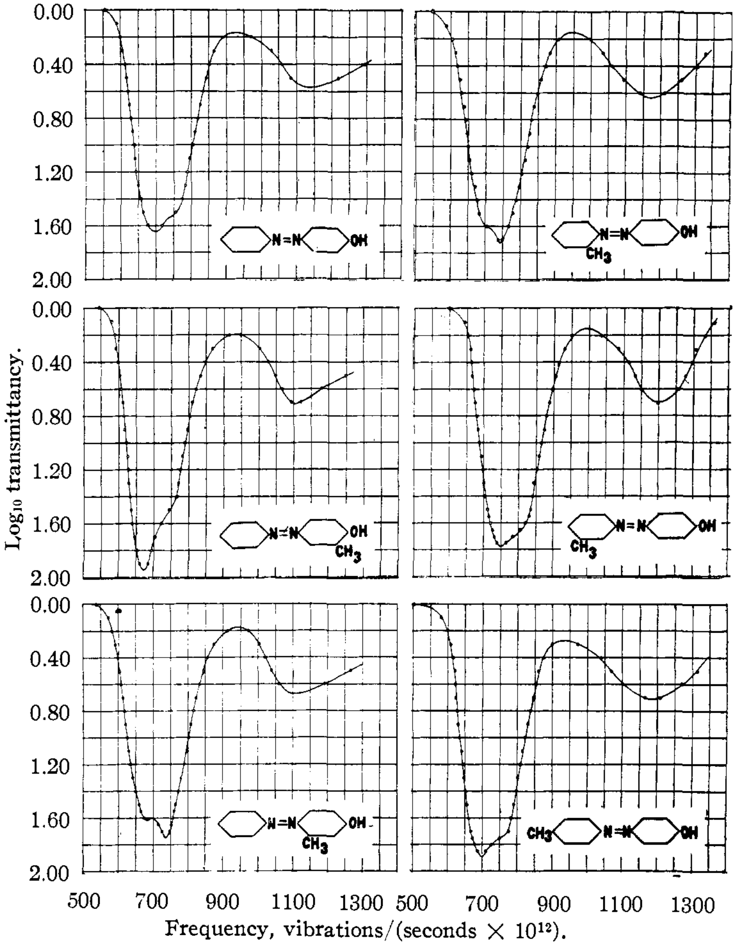

Fig. 1.—The absorption spectra of benzene-azophenol and its monomethyl derivatives in a 3% aqueous solution of sodium hydroxide. Concentration: benzene-azophenol, 2.88 cg. per liter; the monomethyl derivatives, 3.38 cg. per liter; cell thickness in all cases 0.5 cm. Top left, (Ph); top right, (*o'*); middle left, (*o*); middle right, (*m'*); lower left, (*m*); lower right, (*p'*). For explanation of symbols, see Table I.

although the intensity or frequency may be shifted, the mathematical relation between the bands and their general shape when calculated to the same intensity of absorption is the same. Assuming that the two bands which make up the principal band in Figs. 1 and 2 have the same shape in all cases, an analysis of the curves into these components is possible and only one set of curves answering this requirement can be constructed.[12] It is found that approximately the same mathematical relations with regard to frequency exist between the components of the principal bands. These facts tend to justify the assumption that the curves are composed of but two similar components. Whether or not

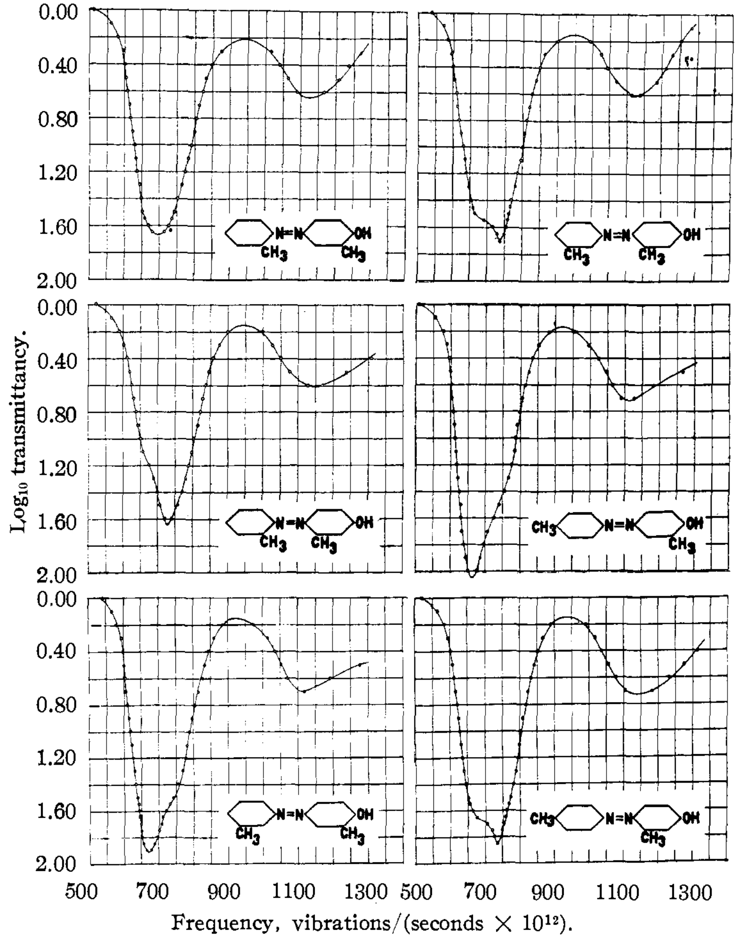

Fig. 2.—The absorption spectra of dimethyl substituted derivatives of benzene-azophenol in a 3% aqueous solution of sodium hydroxide. Concentration: 3.38 cg. per liter; cell thickness, 0.5 cm. Top left, (*o'-o*); top right, (*m'-m*); middle left, (*o'-m*); middle right, (*p'-o*); lower left, (*m'-o*); lower right (*p'-m*). For explanation of symbols, see Table I.

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[12] Brode, *Proc. Roy. Soc. London,* **118A,** 290 (1928).

this assumption is true, their shape gives that appearance and the data obtained by the analysis afford a better expression of the changes in the principal bands than the curves themselves.

In Table I are given both the observed and calculated values of the components of the principal absorption bands. The observed values are indicated by A and B, corresponding to the low and high frequency components, respectively, and the calculated values are similarly designated by A′ and B′. It may be seen that the general direction of the deviations is the same in both cases. Fig. 3 (1) gives the sum of the absorption values of the components (A′ + B′). As has been noted in other solvents and compounds, substitution in the *p*′-position results in an increase in the intensity of the absorption bands and this generalization holds equally true in the case of aqueous sodium hydroxide as a

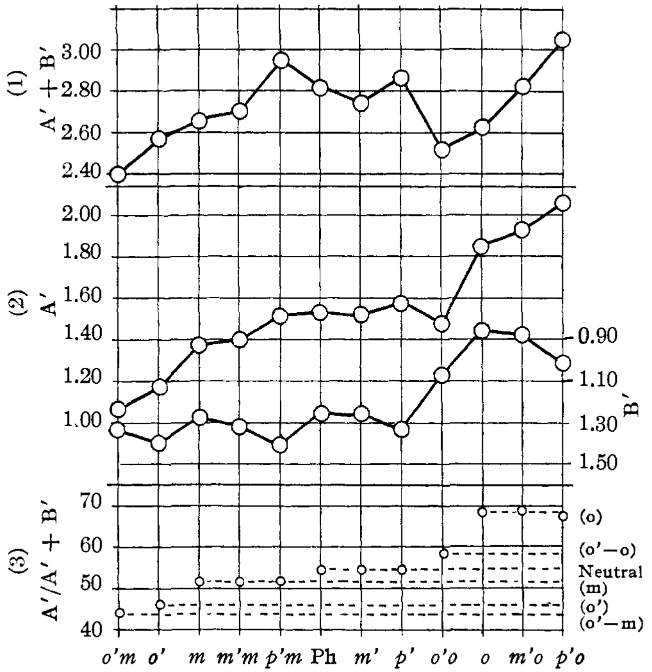

Fig. 3.—(1) Absorption intensities of the sum of the component bands (A′ + B′) of the principal band observed in a 3% aqueous solution of sodium hydroxide. Concentration, 1.5×10^{-4} mole per liter; cell thickness, 0.5 cm. Abscissas in $-\log_{10}$ transmittancy. (2) Absorption intensities of the principal band observed in a 3% solution of sodium hydroxide. A′ = upper series, B′ = lower series. Abscissas in $-\log_{10}$ transmittancy. (3) Percentage of the A′ component of the principal band in a 3% aqueous solution of sodium hydroxide. (The abbreviated symbols for the compounds are explained in Table I.)

solvent. Also substitution in the *o*′-position tends to decrease the intensity of the bands as well as to influence the ratio between the A and B components.

In the absorption spectrum of benzene-azophenol, the parent substance of this series, in an aqueous solution of sodium hydroxide, there is what we may call a neutral equilibrium, in which band A is slightly more intense than band B. This neutral equilibrium does not represent an equal amount of the two forms and may undoubtedly be influenced by changes in the character of either the basic substance or the solvent.[9] For example, in the absorption spectrum of benzene-azophenol in an alcoholic solution of sodium hydroxide, the equilibrium has been shifted, with an increase in B and a corresponding decrease in A. Two other curves closely resemble the neutral curve of benzene-azophenol, namely, those of the *m*′- and *p*′-substituted compounds (Fig. 1). These two, together with the unsubstituted parent substance, constitute the neutral group or series. In the case of the *m*′-substituted compounds, there appears to be practically no effect of any kind on either the equilibrium or the intensity of the A and B bands. In the case of the *p*′-substituted compounds there is an increase in the intensity of absorption, but the relative shapes of the bands and the ratio between the components A and B are the same as in the original compound without the *p*′-substitution.

Substitution in the *o*-position (ortho to the hydroxyl group) (Fig. 1) causes a marked increase in the A band and a corresponding decrease in the B band or, in other words, a shift of the equilibrium toward the A state.

Substitution in the *m*-position (meta to the hydroxyl group) causes a shift of the equilibrium in the opposite direction, that is, an increase in the B band with a corresponding decrease in the A band. The degree of shift of this equilibrium from the neutral state, however, is not as great as in the case of the *o*-substitution.

Substitution in the *o*′-position causes an increase in the B component with a corresponding decrease in the A component, producing a relation differing from the neutral ratio by about the same amount, but in the opposite direction, as that caused by the *o*-substitution. In addition there is a suppression of both bands so that the sum of the intensities of A and B is considerably smaller than in the other cases (Fig. 3 (1)).

The general effect of disubstitution on the intensities of the two component bands is a combination of the effects produced by the two separate directing forces. In the case of the *o*′,*o*-substituted compound (Fig. 2) the effects of the two substituting groups are opposite in character and to a large extent neutralize each other. The *o*-substitution appears to have a slightly stronger influence than the *o*′-substitution as the intensity of the A component present is slightly greater than in the neutral equilibrium. The effect of the *o*′-substitution, however, on the suppression of the bands seems to be only slightly influenced by the oppositely directed force of the *o*-substitution. In the *o′,m*-substituted compound the substituting positions influence in the same direction from the neutral equilibrium or level, so that there is an addition of the two effects and a slightly greater suppression of the bands, due to the *o′*-substitution. The effect of the introduction of the second substitution in the *m′*-position on the absorption spectrum of the compound is practically nil within the accuracy of the observations. There is possibly a slight increase in the intensity of the bands of the *m′,o*-substituted compound above those of the *o*-substituted compound alone and a slight lowering of the ratio of A to B. In the absorption spectrum of the *m′,m*-substituted compound there is an indication of the same effect, although it is less prominent than in the *m′,o*-substituted compound. The influence of the substitution in the *p′*-position, as mentioned before, seems to be merely to increase the intensity of absorption, an effect quite independent of the solvent used.

In the graph (Fig. 3 (2)) giving the intensities of absorption of components A′ and B′, those of B′ are plotted on an inverted scale, since from general observation it may be seen that as one band increases the other decreases. It is to be noted that in cases which are normal, such as the unsubstituted, *m*-substituted and *m′*-substituted compounds, approximately the same differences exist between the A′ and B′ values in the graph. Cases in which there is an intensification of the bands, *p′*-substituted compounds, show a difference greater than normal values, and cases with suppressed bands, *o′*-substituted compounds, show differences smaller than the normal values.

A comparison of the sums of the calculated values of the intensities of the A′ and B′ bands (Fig. 3 (1)) with those of the principal bands of these same compounds in other solvents[9] shows that the same general relations exist in regard to the intensities of the absorption bands. This lends confirmation to the theory that, in any particular compound, the equilibrium between the concentration of the tautomeric forms represented by the bands A and B is directly proportional to the intensities of their absorption bands (A′ and B′).

The ratio of A′ to (A′ + B′) should, therefore, give approximately the percentage of the (A) tautomeric compound present and at the same time make the necessary corrections or allowances for the *p′*- and *o′*-effects on the intensities of both the component bands. (Fig. 3 (3)) gives these percentage values which, as may be observed, can be arranged in groups representing different stages or levels in the equilibrium. The highest percentage is about 68% of the A compound, which may be called the *o*-level. The next stage is that of a neutralized effect from two different levels which exert their influences in opposite directions from the neutral level; this is the combined effect of the *o*- and *o*′-substituting groups. The influence of the *o*-substitution is apparently somewhat stronger than that of the *o*′-substitution, so that the level of this stage is still above the neutral level.

The next level is that of neutrality and is at about 55% of A under the conditions observed. As has been mentioned before, the use of other solvents for the alkaline reagent may shift this level or equilibrium. In the neutral level are the mono-substituted, *m*′- and *p*′-compounds, as well as the parent substance.

The effect of the *m*-substitution is not as strong as that of either the *o*- or the *o*′-substitution. In the cases observed the equilibrium level has been lowered to about 51% of A.

The *o*′-substituted compound, when not influenced by other substitutions, produces an equilibrium at about 44% of A. The effect of the *o*-substitution on the *o*′-substituted compound has been mentioned, and in the case of the *o*′,*m*-disubstituted compound, where both groups tend to lower the percentage of A in the equilibrium, the effect is additive, giving an equilibrium level at 41% of A.

The author wishes to express his appreciation of the help and suggestions given by W. D. Appel of the Dye Laboratory of the Bureau of Standards.

Summary

Benzene-azophenol and the eleven possible mono- and dimethyl derivatives, in which not more than one methyl substitution occurs in a benzene ring, have been prepared and their absorption spectra measured in a 3% aqueous solution of sodium hydroxide in the visible and ultraviolet regions of the spectrum to about 1250 to 1400 f.

From these data the following generalizations have been made.

1. The principal absorption bands appear to be composed of two component bands which, added together, produce the observed bands.
2. The equilibrium between the two components of a band is dependent on the nature of the solvent and the position of the substituting group. An *o*-substitution of the methyl radical in the benzene-azophenol molecule results in an increase in the lower frequency component, with a corresponding decrease in the higher frequency component. A *m*- or *o*′-substitution produces a reverse effect, while the equilibrium is not affected by either a *m*′- or *p*′-substitution.
3. Substitution of a methyl radical in the *p*′-position in benzene-azophenol causes an increase in the intensity of the absorption bands, irrespective of the type of solvent.
4. Substitution of a methyl radical in the *o*′-position in benzene-azophenol causes a decrease in the intensity of the absorption bands.

The data suggest the possibility of a method of structural analysis for the determination of the position of a substituting group in a complex molecule, and a reverse of this in the prediction of the absorption spectra of compounds of known formula and structure. Additional data on the effects of substituting groups, including those of nitro,[13] chlorine and bromine substitutions, are now being collected with this object in view.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A METHOD FOR THE QUANTITATIVE ANALYSIS OF TIN IN ORGANIC COMPOUNDS

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Introduction

In connection with studies on organotin compounds a need was felt for a convenient method for the quantitative estimation of total tin. The successful method described recently by Gilman and Robinson[1] for the estimation of total lead in organolead compounds suggested a similar technique for the analysis of tin. That method, applied to non-volatile organolead compounds, involved decomposition with concentrated sulfuric and nitric acids in the open. It was soon found to be without value when applied to a variety of alkyl tin compounds because of loss due to spattering and volatilization. We have shown that the method is applicable to the analysis of essentially non-volatile organotin compounds, and prior to our analytical studies Krause and Becker[2] used fuming sulfuric and fuming nitric acids for the analysis of some *aryl* tin compounds.

The obvious convenience of carrying out the analysis in open dishes directed efforts to find reagents that would decompose *all* organotin compounds without risk of losing any of the sample as a consequence of spattering or volatility due to vigorous decomposition incidental to the formation of stannic oxide. Several reagents were tried.[3] A satisfactory

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[13] Brode, *Ber.*, **61**, 1722 (1928).

[1] Gilman and Robinson, THIS JOURNAL, **50**, 1714 (1928).

[2] Krause and Becker, *Ber.*, **53**, 178 (1920). In an article which has just appeared, Fichter and Herzbein, *Helv. Chim. Acta*, **11**, 562 (1928), analyzed tin dichlorodiacetate by hydrolyzing the aqueous solution of the compound with ammonia and ammonium nitrate.

[3] One of these involved a *preliminary* decomposition by concd. hydrochloric acid, followed by the nitric–sulfuric acid oxidation to stannic oxide. In this method the compound is first dissolved in carbon tetrachloride, which is an excellent solvent for organotin compounds. The preliminary decomposition by hydrochloric acid is slower than the preliminary decomposition by bromine. However, satisfactory results were obtained by this method with the few compounds tried. We prefer the bromine method that is more fully described in this paper.