whose precipitabilities plotted against their dilute solution viscosities lie on the same curves which are characteristic of the original *linear* polyesters. Hence, the relation between dilute solution viscosity and solubility is not sensitively affected by branching. (However, the relations of these properties to molecular weight are apparently changed.)

Further, actual thermosetting of polyester plastics and vulcanization of polyester rubbers is shown, by viscosity and creep experiments, to follow from these simple free-radical reactions. Similar processes are suggested for aging, "oxidation" and other reactions of chain polymers containing little or no olefinic unsaturation.

MURRAY HILL, N. J. RECEIVED NOVEMBER 27, 1946

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

A Spectrophotometric Study of the Hafnium–Alizarin Lake

BY HERMAN A. LIEBHAFSKY AND EARL H. WINSLOW

The constitution of hydroxyanthraquinone lakes has always been a lively topic—in the beginning, because of the relation of these lakes to mordant dyeing, and more recently in connection with their formulation as chelate compounds. As a sequel to earlier work,[1] we have studied spectrophotometrically the formation of the hafnium–alizarin lake, which is so stable in acid solution that it serves well for the estimation of hafnium. Needless to say, the problem is exceedingly complex, not only owing to the nature of the reactants but also because the lakes as finally measured are colloidal suspensions. These complications should tend to disappear with increasing dilution, and there is consequently some hope of obtaining results simple enough to be interpreted from work on a microgram scale; but one can scarcely expect definitive answers to all the questions involved. The experimental method has already been described.[1]

Lake formation was investigated under three sets of conditions: (1) with hafnium in excess (Fig. 1), (2) with hafnium and alizarin comparable (Fig. 2), (3) with alizarin in excess (Figs. 3 and 4), the last being the standard condition for the spectrophotometric estimation of hafnium. The principal evidence on the constitution of the lake in question will be obtained by using derived data from Figs. 1 and 3 to interpret Fig. 2, in which the

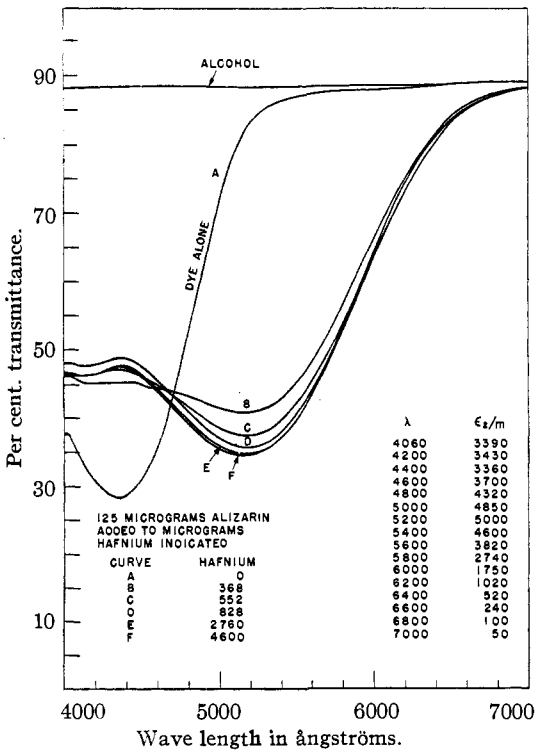

Fig. 1.—Transmission curves for lake formation with hafnium in excess.

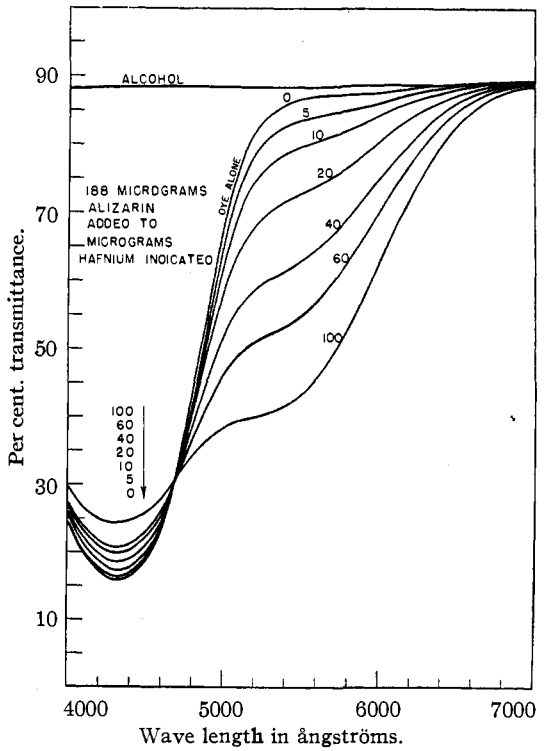

Fig. 2.—Transmission curves for lake formation with hafnium and alizarin comparable.

(1) Liebhafsky and Winslow, THIS JOURNAL, 60, 1776 (1938).

progress of lake formation can be followed by the decreasing absorption due to alizarin (4360 Å.) and the increasing absorption due to the lake (5600 Å.).

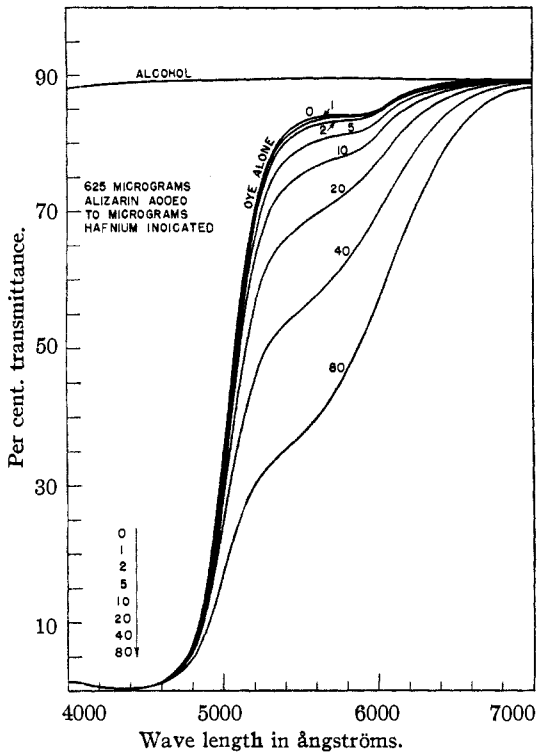

Fig. 3.—Transmission curves for lake formation with alizarin in excess.

To interpret the results, it will be assumed that lake formation was virtually complete under each set of limiting conditions. By way of justification, we point out that, at the one limit, Beer's law governs the amount of lake formed with the alizarin in excess (Fig. 4). At the other limit, there can be little alizarin remaining uncombined in the two experiments showing maximum lake formation (Fig. 1), for the corresponding curves show no absorption maximum near 4360 Å.; furthermore, their coincidence indicates that further addition of hafnium would not have increased the light absorption due to the lake. (Unfortunately, the volume in which the lake was formed increased from 0.7 to 7 cc. as the amount of added hafnium was increased from 368 to 4600 micrograms, and the hydrogen ion concentration increased also; these facts may weaken the second argument.) It will be assumed also that the molecular extinction, ϵ_2, and the composition of the lake are identical under the three sets of conditions.

If the formula of the lake is abbreviated to $(Hf)_m(Az)_n$, the problem is the determination of n/m. According to the line for 5600 Å. in Fig. 4, $4.3(10^{-7})$ moles is the maximum amount of hafnium combined as lake with the $5.2(10^{-7})$ moles of alizarin used in the experiments of Fig. 1; whence $n/m = 1.2$ for the $4.3(10^{-7})/m$ moles of lake involved.

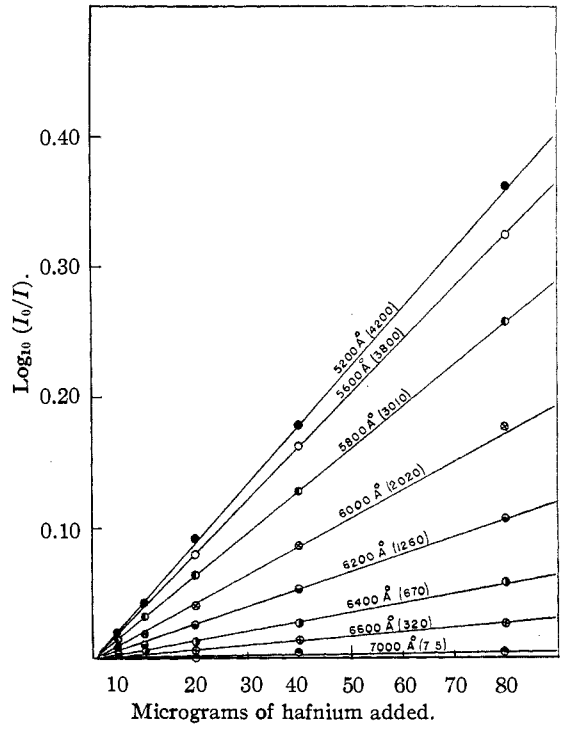

Fig. 4.—Beer's law plot for Fig. 3.

To interpret Fig. 2, values of ϵ_2/m are required from Fig. 1. These were calculated from Fig. 1, curve E according to the equation

$$\log_{10}(I_0/I) = \epsilon_2(5.15)\ 4.3(10^{-7})/0.027\ m \qquad (1)$$

I_0 and I are, at each wave length, the transmitted intensities (transmittances) for alcohol and for the suspended lake; 5.15 is the cell length in cm., and 0.027 liter, the volume of material prepared for measurement. The calculated results are given in Fig. 1.

When alizarin and lake are both present, Beer's law may be written

$$\log_{10}(I_0/I) = \epsilon_1(\Sigma[\mathrm{Az}] - n[\mathrm{L}]) + \epsilon_2[\mathrm{L}] \qquad (2)$$

if the cell is of unit length. Here ϵ_1 is the molecular extinction of alizarin; the brackets denote moles/liter; $\Sigma[\mathrm{Az}]$ indicates alizarin added, and L represents the lake. Differentiating equation 2 after dividing by m gives

$$d\log_{10}(I_0/I)/d(m[\mathrm{L}]) = -n\epsilon_1/m + \epsilon_2/m \qquad (3)$$

Now, $m[\mathrm{L}]$ is the concentration of combined hafnium, which has been assumed calculable from Fig. 4. $\mathrm{Log}_{10}I_0/I$ plotted against this combined hafnium as abscissa should, according to equation 3, give at each wave length a straight line from the slope of which n/m can be calculated if ϵ_1 and ϵ_2/m are known.

The data from Fig. 2 are plotted in Fig. 5, where the calculated n/m values are also given. (The ϵ_1 values (Fig. 6) used in these calculations

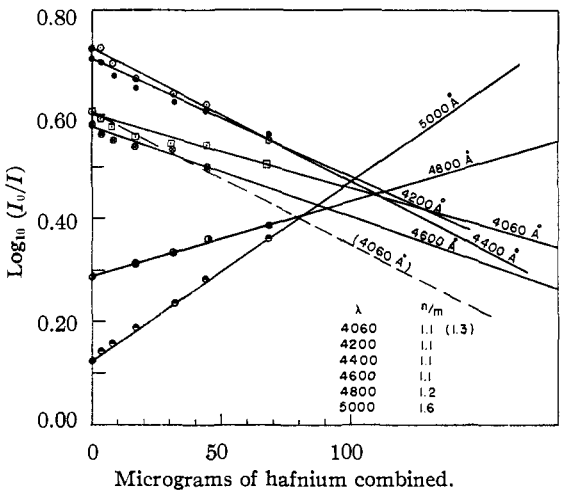

Fig. 5.—Determination of combining ratio, n/m, for the hafnium-alizarin lake.

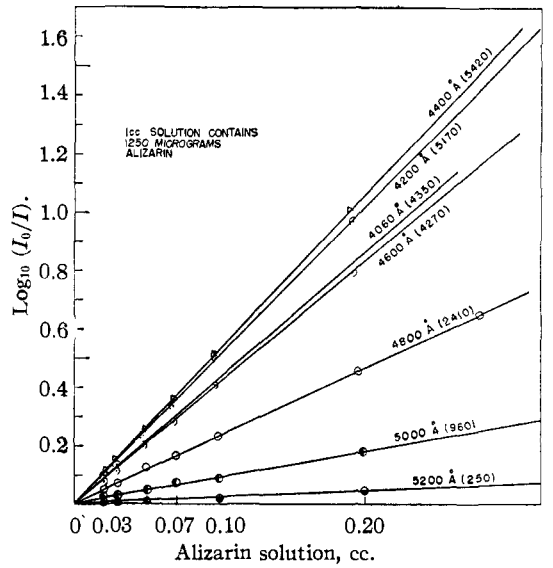

Fig. 6.—Beer's law plot for alizarin in alcohol.

were obtained on solutions of alizarin in alcohol.) The data fall along straight lines—especially at the longer wave lengths—about as well as could be expected; the n/m values are in good agreement with 1.2, which was deduced from Fig. 1. Owing to the greatly different ratios of hafnium to alizarin in Figs. 1, 2 and 3, we doubt whether the excess of n/m above unity indicates adsorbed alizarin. In other words, the lake appears to contain hafnium and alizarin combined in equimolal amounts, and the excess of n/m above unity is probably due to experimental error or to an over simplification in the basic assumptions.

In Fig. 5, $n/m = 1.3$ was calculated from the slope of the dotted line for 4060 Å., which shows that n/m is not very sensitive to a change in slope at these wave lengths. As the wave length increases, however, it soon becomes impossible to obtain reliable n/m values from the data. At both 4060 and 5000 Å., for example, a 12% decrease in ϵ_2/m will reduce n/m approximately to unity, though Fig. 5 gives 1.6 for the latter wave length and only 1.1 for the former.

It is scarcely worth while to discuss all the possible uncertainties in the experiments or in their interpretation. We shall point out only that the extinction coefficients as calculated include scattered light; in this connection, see ref. 1, Fig. 11. Such scattering could be greatest under the conditions of Fig. 1, which would make the ϵ_2/m values too high relative to Figs. 2 and 3; this could have cause n/m to exceed unity.

Values of ϵ_2 were calculated from the data of Fig. 4, m being taken as unity and I_0 being taken as the transmittance of the alizarin solution. These values are given in parentheses (Fig. 4) for comparison with the ϵ_2/m results in Fig. 1. By and large, the differences are not serious.

Incomplete Lake Formation.—For the experiments of Fig. 2, the amounts of hafnium combined, as calculated from Fig. 4, are in every case less (by 15 to 30%) than the amounts added. The "equilibrium quotients" (moles of lake divided by the product of moles of uncombined hafnium and moles of free alizarin), which were expected to show the completeness of lake formation, varied unsystematically from $3(10^6)$ to $8(10^6)$. In the case of Fig. 1, similar calculations indicated the presence of more free alizarin than the shape of the curves (near 4360 Å.) with added hafnium would permit.

The conditions obtaining during lake formation are so complex that we are inclined to give these calculations little weight. If they mean anything at all, they indicate that the equilibria are "frozen" when the lakes are acidified. It will be recalled[1] that the lakes are formed in a minimum volume of ammoniacal solution containing ammonium ion; that the addition of hydrochloric acid in excess is carried out after the lakes have had two minutes in which to form; that dilution with alcohol to 27 cc. follows immediately; and that the lakes as finally suspended show little or no tendency to dissociate and are stable toward hydrogen ion (but not toward sulfuric acid—see below).

During lake formation, the β acid-hydrogen of the alizarin is largely dissociated; Hüttig[2] has shown the two dissociation constants at 18° to be $1.14(10^{-12})(\alpha)$ and $6.6(10^{-9})(\beta)$. To judge the condition of the hafnium, we may use information about zirconium,[3] for the two elements are virtually identical in chemical behavior. Although hafnyl ion, HfO^{++}, is the principal substance in the acid stock solution, hafnyl hydroxide (amphoteric) and derived species must be assumed present while the lake is forming. The substances then actually reacting are unknown, and they need not

(2) Hüttig, *Z. physik. Chem.*, **87**, 129 (1914).

(3) Venable, "Zirconium and its Compounds," Chemical Catalog Co., Reinhold Publ. Corp., New York, 1922.

be the principal species present; in any case, the concentrations of these actual reactants will become very small as lake formation proceeds under the conditions of Fig. 2. It is consequently not surprising that the process should stop short of completion.

Effect of Sulfuric Acid.—The repressive effect of sulfuric acid on the formation of the zirconium-alizarin lake is well known.[4] With hafnium, the action of 12 *N* sulfuric acid on lakes formed in the usual manner was compared with that of 12 *N* perchloric (Fig. 7), the acids being added before the dilution with alcohol. In the former case, the eye could observe a rapid disappearance of the lake; in the latter, no visible change occurred. The conclusions from these and other experiments are: (1) The hafnium (or zirconium) lake cannot be decomposed by the simple action of hydrogen ion, as are the lakes of most other cations (*e. g.*, Fe^{+++})[5]; (2) the effect of the sulfuric acid must be traced to its action on the hafnyl ion.

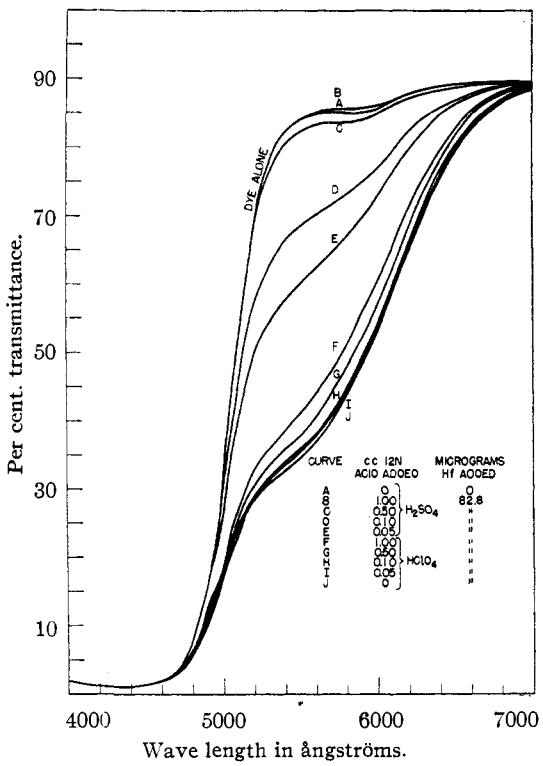

Fig. 7.—Contrasting effects of sulfuric and perchloric acids on lake formation.

That sulfuric acid forms stable complexes with zirconyl ion is well known.[3] Since HSO_4^- is a relatively weak acid, it is entirely logical to assume that sulfuric acid attacks the lake because hafnyl (or zirconyl) acid sulfate is a very stable complex (*cf.* ref. 3, p. 81). Whether or not the complex has this formula, however, the important point for the present argument is that the peculiar effectiveness of sulfuric acid in decomposing the hafnium (zirconium) lakes is not primarily due to the great stability of formula A, Fig. 8, for which the dissociation constant is $1.14(10^{-12})$ at 18°. On the other hand, the stability of this hydrogen-bonded chelate ring must be the predominant factor in the decomposition by hydrogen ion of the lakes of most other cations.[6]

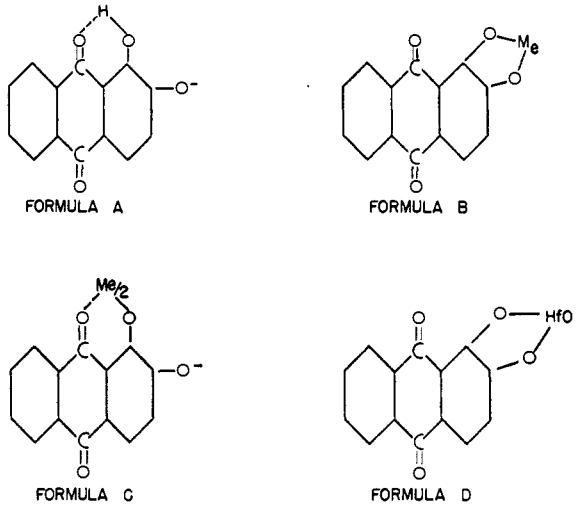

Fig. 8.—Illustrative structural formulas (primary and secondary valences have been differently designated only to emphasize that the electrons of the bond are both contributed by a single atom in the latter case): —, primary valence; - - - -, secondary valence; Me = 2 equivalents.

Formula of the Lake.—Only the minimum requisite to our argument of the controversial attempts to assign formulas to the mordant-dye lakes will be given here. Liebermann[7] and Werner[8] were both inclined to regard them as definite compounds containing chelate rings,[9] but rings of different types. Liebermann favored those in which the metal ion was bound by two principal valences (formula B), while Werner maintained that "inner complex" formation (one primary, one secondary—or coördinating—valence; formula C) was involved. Even today,

(4) See ref. 1, in which read "greater" for "less" in the last line of text on p. 1778. The conclusion that lake formation was the greater with ammonium hydroxide added was based on the transmittance readings immediately following, which were taken only at 5600 Å. These experiments were repeated with hafnium, and complete curves were obtained. These curves showed that the lake formed in the alkaline solution scattered much more light than that formed in the presence of sulfuric acid (*cf.* ref. 1, Fig. 11); consequently, scattered light could easily have accounted for the difference observed in the case of zirconium. The conclusion is, therefore, that the repressive effect of sulfuric acid on lake formation is the same whether or not ammonium hydroxide is added.

(5) Weinland and Binder, *Ber.*, **47**, 977 (1914).

(6) Liebhafsky, *J. Chem. Ed.*, **23**, 341 (1946).

(7) Liebermann, *Ber.*, **26**, 1574 (1898).

(8) (a) Werner, *Ber.*, **41**, 1062 (1908); *cf.*, however, the carefully worded paragraph about "adjective dyes" in (b) "New Ideas on Inorganic Chemistry," Longmans, Green, and Co., London, 1911, p. 225.

(9) For a valuable summary, *cf.* Diehl, *Chem. Rev.*, **21**, 39 (1937), whose terminology is employed above.

Biltz's[10] skeptical attitude seems justified, for Weiser and Porter[11] have concluded that the lakes in question are not definite compounds at all, being held together merely by adsorption forces.

The spectrophotometric evidence as interpreted here shows that hafnium and alizarin form a definite compound, held together by valence forces, the combining ratio being 1/1. There appears to be little or no adsorption of excess dye. The conditions investigated, however, are not those of mordant dyeing.

The definitive formula of the hafnium–alizarin lake cannot be adduced from the evidence available. But formula D, analogous to formula B, is extremely plausible for the following reasons. (1) The combining ratio: that alizarin and hafnium should combine in equimolal amounts contrasts with the evidence for other lakes; *e. g.*, three moles of alizarin combine with one of ferric ion.[5] Consequently, different types of chelate rings could be involved in the two cases, the "inner complex" type (formula C) being characteristic of the latter. (2) Type of bond: the strong tendency of hafnyl ion to combine with anions (*e. g.*, HSO_4^{--}, F^-) indicates that its salt-forming (coulombic) characteristics are strong relative to its coördinating (homopolar) tendency; ferric ion, being derived from a transition element, should show a relatively greater tendency toward coördination. (3) Acid stability: the failure of hydrogen ion to decompose the alizarin lake of hafnium (or zirconium) contrasts sharply with its effectiveness toward the lakes of most metals, which suggests that the two classes be assigned different formulas. It is logical to assume that the ferric lake, for example, is thus decomposed because formula A is a more stable structure than are inner complex rings like formula C; this points to formula D for the hafnium–alizarin compound.

Because of its tendency to form inner complex salts, cupric ion was recently selected by Calvin and Wilson[12] for a study of the stability of this type of ring. (A parallel investigation of zirconyl or hafnyl ion would be very interesting.) The curves in ref. 1, Fig. 7, show that the solvated cupric ion (absorption near 7000 Å.) exists in acid solution beside the zirconium–alizarin lake; though the amount of copper greatly exceeded that of zirconium, there was no evidence that it contributed to lake formation (the yellow cupric chloride complex did, of course, form; *cf.* curve D near 7000 Å.). This contrast in the behavior of cupric and zirconyl ions reinforces the argument for formula D.

Summary

Spectrophotometric evidence has been obtained to show that the hafnium–alizarin lake is a definite chemical compound, the two constituents being combined in equimolal amounts. There appears to be little or no adsorption of excess dye.

Under some conditions, lake formation is incomplete.

On the basis of the evidence available, the hafnium lake has been assigned a chelate-ring formula different from the "inner complex" type of chelate ring usually assumed for the lakes (such as that of ferric ion) unstable toward acid.

(10) Biltz, *Ber.*, **38**, 4143 (1905); especially the last paragraph.

(11) Weiser and Porter, *J. Phys. Chem.*, **31**, 1824 (1927).

(12) Calvin and Wilson, THIS JOURNAL, **67**, 2003 (1945).

SCHENECTADY, NEW YORK RECEIVED NOVEMBER 1, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Electric Moments of Ortho-substituted Phenols and Anisoles. III. Nitriles and Anils[1]

BY COLUMBA CURRAN[1a] AND E. P. CHAPUT

The electric moments of *o*-halophenols in carbon tetrachloride[2] have been interpreted as revealing the presence of intramolecular OH---X bonds, some of which are broken when these compounds are dissolved in dioxane. The intramolecular OH---O bonds in such compounds as guaiacol and salicylaldehyde appear to remain unbroken in dioxane, indicating that in ortho-substituted phenols the O—H---O bridge is stronger than the O—H---X bridge.[3] In the ortho-substituted anisoles studied to date the methoxy group appears to be locked in a configuration having the methyl group *trans* to the ortho substituent.

In the present investigation the O—H---N bridge in five and six-membered rings was studied by analyses of the electric moments of salicylonitrile and substituted salicylideneanils and their methyl ethers. The bond angles and bond moments assumed in earlier investigations were again used in obtaining moments calculated for various configurations, and additional moments selected from the literature are indicated in the discussion.

Experimental

Preparation and Purification of Compounds.—Salicylonitrile was prepared by treating salicylaldehyde with hydroxylamine hydrochloride to form the oxime, refluxing

(1) Presented before the Physical and Inorganic Division at the Detroit meeting of the American Chemical Society, April, 1943.

(1a) Brother Columba Curran, of the Congregation of Holy Cross, Notre Dame, Indiana.

(2) Anzilotti and Curran, THIS JOURNAL, **65**, 607 (1943).

(3) Curran, *ibid.*, **67**, 1835 (1945).