NOTES

The Ionization of Certain Bisphenols

By Walter Mahler

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A spectrophotometric investigation of phenolic compounds, especially the substituted bisphenols, was instituted in order to permit a more specific identification and determination of these substances. In the course of this study ultraviolet absorbancy at a given wave length was measured as a function of changing pH values. The wave length chosen for each compound was one which gave a large difference in absorbancy between the undissociated and ionized form. The results suggested the usefulness of the procedure for measuring the ionization constants of the chlorine substituted bisphenols. The validity of ultraviolet spectrophotometry as a method of measuring ionization has been demonstrated.[1]

The curves correspond to the equations

$$K_1 = \frac{(H^+)(HA^-)}{(H_2A)} \text{ and } K_2 = \frac{(H^+)(A^=)}{(HA^-)}$$

where K_1 and K_2 are the first and second ionization constants. The plateaus of the absorption curves correspond to the un-ionized (H_2A), singly ionized (HA^-) and doubly ionized species ($A^=$).

The absorbancy data are shown in Fig. 1. The ionization constants as calculated from the equations are listed in Table I. Measurements were made with a Beckman model DU spectrophotometer using 1-cm. silica cells and employing concentrations of 0.02 mg. of compound per ml. of aqueous solution at 20 ± 0.5°. The first ionization of the bis-trichlorophenol in water was unobtainable because of the very low solubility of that compound in the undissociated state.

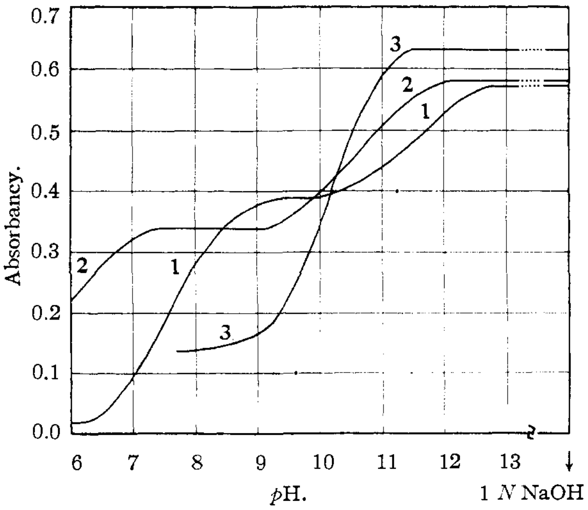

Fig. 1.—0.020 mg./ml. in water; buffer, 0.05 M borate–boric acid: 1, 2,2′-methylene-bis-(4-monochlorophenol) wave length 305 mμ; 2, 2,2′-methylene-bis-(4,6-dichlorophenol) wave length 305 mμ; 3, 2,2′-methylene-bis-(3,4.6-trichlorophenol) wave length 320 mμ.

Table I

Compound	pK_1	pK_2
2,2′-Methylene-bis-(4-monochlorophenol)	7.6	11.5
2,2′-Methylene-bis-(4,6-dichlorophenol)	5.6	10.65
2,2′-Methylene-bis-(3,4,6-trichlorophenol)		10.1
2,2′-Methylene-bis-(3,4,6-trichlorophenol)[a]	5.4	10.85

[a] In aqueous solution containing 30% methyl alcohol.

It is interesting to note that the plateau corresponding to the singly ionized species does not necessarily lie at one-half the absorbancy value for the doubly ionized.

Both a hyperchromic and hypochromic effect may be attributed to the presence of an intramolecular hydrogen bond of charge–dipole nature in the monovalent ion. A dipole–dipole intramolecular hydrogen bond has been found in similar bisphenols by infrared data in the un-ionized form of the molecule.[2,3] The large difference in pK_1 and pK_2 (Table I) confirms the expectation of even stronger interaction between an ionized and un-ionized hydroxyl group of requisite proximity.[4]

The two benzene rings of the molecule are not in the same plane.[5] The hydrogen bond, operating across the space between the rings will exert a pull on the oxygen atom directed out of the plane of the benzene ring. The result however will not be actual destruction of coplanarity (*i.e.*, resonance) of the chromophoric oxygen with its benzene ring, but the characteristic transitions will be limited to vibrational states in which the bonds are extended to permit coplanarity. The reduction of the number of allowable transition states leads to a decrease in intensity of absorption. This is identical to the effect attributed to slight steric hindrance tending to decrease the planarity of a conjugated system.[6]

The intramolecular hydrogen bond will also decrease the solvation of the monovalent ion relative to the strong solvation of the divalent ion where no such intramolecular bond can exist. (These bisphenols are extracted from dilute aqueous alkali by organic solvents although they are not in the class of the sterically hindered phenols.)[7] The decrease in relative solvation due to intramolecular hydrogen bonding is analogous to decrease in solvation due to less polar solvents.[8] Accordingly a relative increase in intensity of absorption may be attributed to this aspect of the intramolecular hydrogen bond. This increase is more important for

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[8] L. N. Ferguson, *Chem. Revs.*, **43**, 385 (1948), and references.

the less substituted compounds and correlates directly with the difference of spectra in polar and non-polar solvents.

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Preparation and Properties of the Rare Earth Fluorides and Oxyfluorides

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Although fluorine and anhydrous hydrogen fluoride have been successfully used in the preparation of the rare earth fluorides, comparatively little work has been done on the fluorination of rare earth compounds with halogen fluorides. A recent qualitative study[1] has indicated that chlorine trifluoride and bromine trifluoride react with the rare earth oxides and oxalates and that the reaction seems to depend on the amount of moisture absorbed by the rare earth compound previous to fluorination. Since chlorine trifluoride is easily available and is comparatively easy to handle, it was decided to investigate its reactions with the rare earth oxides in greater detail.

Only the oxyfluorides of lanthanum,[2] yttrium,[2b] cerium[3] and holmium[4] are mentioned in the literature. Of these, the first two were prepared by a high temperature reaction between the corresponding oxide and fluoride,[2a,3] and the first by hydrolysis of the trifluoride.[2] Since the latter reaction appeared to present the simplest method of preparation, it was used to prepare other rare earth oxyfluorides.

Chemicals.—The rare earths were obtained as oxides from the A. D. Mackay, Inc., or from the Fairmont Chemical Co. They were guaranteed to be 99.8% pure. Whenever possible, the purity was checked by converting the oxides to the respective chlorides, and comparing the absorption spectra of their aqueous solutions with the data of Moeller and Brantley.[5] No impurities were observed in cases of lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium. The available samples of other rare earth oxides were too small to permit an accurate analysis.

Chlorine trifluoride was obtained from the Harshaw Chemical Company in one pound cylinders. It was of technical grade, and probably contained some hydrogen fluoride and chlorine monofluoride as impurities.

Reactions of the Rare Earth Oxides with Chlorine Trifluoride.—The rare earth oxides in a platinum boat were heated in a muffle furnace at 800° for several hours and then quickly transferred to a nickel tube where they were allowed to cool in a current of dry nitrogen. After cooling to room temperature of approximately 25°, the oxides were rapidly weighed, reintroduced into the nickel tube and a slow stream of chlorine trifluoride was passed through the apparatus. After several minutes the chlorine trifluoride was shut off, the reaction tube was flushed with dry nitrogen, and the fluorinated sample was taken out and weighed. The increase in weight due to the conversion $M_2O_3 \rightarrow 2MF_3$, indicated that the reaction, if any, occurred within the first five minutes. No further change in the sample was observed even after passing chlorine trifluoride for one hour.

Only a slight increase in weight of the samples was noticed in the reaction with lanthanum, cerium, praseodymium, neodymium and samarium oxides; on the other hand, gadolinium showed approximately 80% conversion to the fluoride. Dysprosium, erbium, thulium, ytterbium and lutetium oxides showed no increase in weight.

Since in all cases the reaction of chlorine trifluoride was, at least, incomplete, the effect of moisture was studied next. Several drops of water were added to each rare earth oxide sample before it was subjected to fluorination. After the reaction, the sample was weighed and then treated again with water and with chlorine trifluoride. In a few cases the treatment had to be repeated several times before a constant weight of the product could be obtained. The final results were generally reproducible to within 2–3%.

The lighter rare earth oxides, from lanthanum through samarium were, usually, completely fluorinated. The intermediate oxides (Eu_2O_3–Er_2O_3) showed only partial fluorination varying from 80% in the cases of gadolinium, to about 12% for erbium, while the higher oxides did not react at all. In the case of yttrium, the reaction was approximately 45% complete. These results were confirmed by the analysis of the reaction product whenever possible. Since the amount of the heavier rare earth oxides available for this investigation was of the order of magnitude of 10 mg., it was rather difficult to obtain accurate analytical results. The fact that the last members of the lanthanide series did not fluorinate was, however, checked by taking the X-ray powder diagrams of the material after fluorination. In all cases erbium, thulium, ytterbium and lutetium gave the known oxide pattern. The lighter elements on the other hand gave powder diagrams which checked with the known fluoride pattern.

It is seen from the above results that the ease of fluorination decreases with increasing atomic number of the rare earth series. The last members do not undergo any appreciable reaction under the described conditions. This behavior is not surprising since the relative basicity of the oxides decreases in going from lanthanum to lutetium.[6] Although many various reactions have been used in order to establish the sequence of basicities,[7] and the relative sequence is not always the same, it is interesting to note that, on the basis of theoretical considerations, von Hevesy predicted that the basicity of yttrium is intermediate between that of dysprosium and holmium, and the next element, erbium, should be less basic than holmium.[8] The reactivity of yttrium oxide toward chlorine trifluoride is indeed less than that of dysprosium oxide but considerably greater than that of erbium oxide.

Since the rare earth fluorides are insoluble in dilute acids, while the oxides are readily soluble, it is possible that the differences in their reactivities toward chlorine trifluoride may be utilized in the initial stages of the rare earth separation.

Rare Earth Fluorides.—The rare earth fluorides are insoluble in water and in dilute acids either at room temperature, or on boiling. They are slightly soluble in hot concentrated acids and are readily soluble in 0.5 *M* solution of aluminum nitrate, and in 0.1 *M* solution of the disodium salt of ethylenediamine tetraacetic acid, provided, in the latter case, that the solution is neutral or basic.

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