Analogous results have been obtained with hempseed meal.

The data of Smith and co-workers[11] have been interpreted to indicate that the influence of salts on the solubility of soybean proteins in the neutral *p*H range is a parallel phenomenon.

The observations cited are exceptions to the hitherto-accepted generalization that the solvent action on proteins of salts and alkali is additive.

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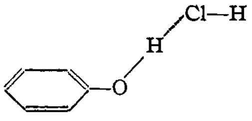
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Increases in the Acid Strength of Hydrogen Chloride in Dioxane Brought about by Phenols and Alcohols

BY PAUL D. BARTLETT AND HYP J. DAUBEN, JR.

Some years ago Meerwein and his co-workers[1] showed that the metallic chlorides which catalyze the rearrangement of camphene hydrochloride into isobornyl chloride are all capable of forming complexes with hydrogen chloride which are stronger acids than hydrogen chloride itself. This property was demonstrated by a method introduced by Hantzsch.[2] A solution of hydrogen chloride in dry ether was made just too dilute (0.02 *N*) to redden the indicator butter yellow (*p*-dimethylaminoazobenzene). The addition of equivalent stannic chloride (which alone at this concentration did not redden the indicator) now turned the indicator red, and a dilution of 120-fold was necessary to restore the yellow color. This was clearly due to the fact that in ether an acid of the type H_2SnCl_6 is stronger than hydrochloric acid. Meerwein concluded that the catalytic activity of the chloride and its acid-strengthening power were closely related manifestations of its complex-forming ability.

By Hantzsch's method it can be shown that the phenols, which also catalyze the rearrangement of camphene hydrochloride, conform to this generalization in that they, too, increase the acid strength of hydrogen chloride in ethereal solution. The effect is much less than with stannic chloride, but quite definite. We are forced to the conclusion that phenols, like the complex-forming inorganic chlorides, can form complexes with hydrogen chloride in which the phenol is attached to the chlorine and encourages the separation of this as an ion. The only probable manner in which a phenol can form such an attachment is through hydrogen-bond formation at its hydroxyl group



and we thus have a method of making some quantitative measurements on the relative tendencies to hydrogen bonding by a series of hydroxyl compounds.

This subject is of particular interest at the present time in view of the attention directed by G. N. Lewis[3,4] to the general aspects of the acid–base relationship. Any molecular species X which can form a coördinate link with the chloride ion, $\mathrm{X}:\overset{..}{\underset{..}{\mathrm{Cl}}}:^-$, is functioning as an "acceptor" center, in the terminology of Sidgwick,[5] while the chloride ion functions as a "donor." Lewis prefers to substitute the terms "acid" and "base" for "acceptor" and "donor," and says of the Sidgwick notation: "This expressive nomenclature I should be glad to adopt if I did not hope to show that his classification coincides absolutely with the classification of acids and bases, so that the need for new names disappears."[3,4]

Now in the present instance we have a substance, a phenol, which can function as an acid in the Brönsted sense by donating a proton to some acceptor; it can also function as an acid in the Lewis sense, as an acceptor, by forming a complex with the chloride ion or with hydrogen chloride through its chlorine. If these two kinds of acidity run completely parallel in a series of phenols, being governed by exactly the same structural features, then we have no need to differentiate between them. However, as we shall show, the Lewis

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[1] Meerwein, Hammel, Serini and Vorster, *Ann.*, **453**, 16 (1927); Meerwein, *ibid.*, **455**, 227 (1927).

[2] Hantzsch, *Z. Elektrochem.*. **29**, 226 (1923); *Ber.*, **58**, 627, 631 (1925).

[3] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[4] Lewis and Seaborg, THIS JOURNAL, **61**, 1886, 1894 (1939).

[5] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, New York, N. Y., 1929.

acidity and the Brönsted acidity do not run completely parallel and much interest is attached to their separation and comparison. Therefore we cannot absorb the one class of acids completely into the other. Rather than to use a new term for proton-donors, which are now generally designated by the term "acid," it seems to us best to retain this term in its accepted sense and to adopt Lewis's second choice by calling the Lewis acids "acceptors." At least this practice will contribute to clarity in the present paper. Ingold's useful term, "electrophilic reagent," is of course synonymous with "acceptor."

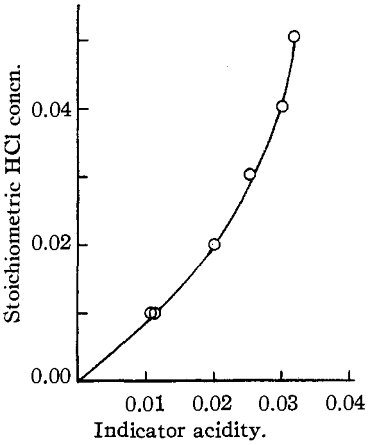

Fig. 1.

For exploring the relationship between acid strength and acceptor activity among the phenols it was desirable to have a quantitative method which should be sensitive to small differences in the latter property. Accordingly, series of colorimetric measurements were made using a one-color indicator, and comparing the specific color intensity of a standard solution of hydrogen chloride with those of weaker hydrogen chloride solutions containing progressively greater concentrations of a phenol. Because of its volatility, ether would be an objectionable solvent for this purpose, and we used carefully purified dioxane instead. As an indicator pentamethoxy red (2,2′,2″,4,4′-pentamethoxytriphenylcarbinol) proved well adapted to our purpose. This indicator turns from colorless to red at such a point that a 0.02030 *M* solution of hydrogen chloride in dioxane is a convenient standard. This standard solution, containing six drops of a 0.005 *M* solution of the indicator in 50 cc. of solution, was compared with series of solutions 0.001578 *M* in hydrogen chloride and from 0.05 to 4.0 *M* in the phenol containing the same amount of indicator. For each phenol–hydrogen chloride solution readings were taken at different times and with thermostatic control, so that temperature effects were eliminated and time effects could be shown to be absent. In each case we established the absence of color in solutions of the phenol and indicator more concentrated than any used in the work.

The expressing of our results in terms of a hydrogen ion activity or H_0 scale[6] is rendered undesirable by the fact that our indicator reaction forms water

$$\underset{\text{Colorless}}{ROH} + BH^+ \rightleftarrows \underset{\text{Colored}}{R^+} + H_2O + B$$

Although our solvent and materials were as anhydrous as possible, it is unjustified to assume that the water formed as a result of this reaction is the only water present. Accordingly, no attempt is made to use a true measure of acidity. The quantity called "indicator acidity" in Fig. 1 is the molarity of hydrogen chloride in the standard solution multiplied by the ratio of color intensities in the test solution and the standard. Figure 1 shows the relationship of this indicator acidity to the stoichiometric concentration of hydrogen chloride in a series of solutions containing no phenol.

Figure 2 shows the plots of indicator acidity against phenol concentration for several phenols studied. These curves are not all the same shape, and do not appear to approach the same limiting value of the ordinate. This is not surprising since we are dealing with a solvent of dielectric constant only 2.2,[7] and adding to it relatively large amounts of substances which will raise the dielectric constant and probably alter the behavior of electrolytes. It can be seen that the early parts of the

TABLE I

COMPARISON OF ACCEPTOR ACTIVITY AND ACID STRENGTH FOR HYDROXYL COMPOUNDS

Compd.	Slope	pK_a
p-Cyanophenol	0.432	7.89
p-Chlorophenol	.097	9.39
o-Chlorophenol	.045	9.11
Phenol	.036	10.00
p-Cresol	.032	10.17
o-Cresol	.0294	10.20
s-Trichlorophenol	.0123	7.59
Methanol	.0085	17.00
Ethanol	.0064	19.14
i-Propanol	.0020	
Acetic acid	.0102	4.73

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[6] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[7] Kraus and Fuoss, *ibid.*, **55**, 21 (1933).

phenol curves are very nearly linear and differ among themselves markedly in slope. This slope of the initial part of the curve of indicator acidity against phenol concentration seems about the best comparative measure of the acceptor activities of the different phenols. We have no way of determining to what extent the slope reflects the acid strength of the HCl–phenol complex as contrasted with the actual extent of conversion of the HCl molecule into the complex. Since these two effects are almost certain to run parallel in any series of closely related hydroxyl compounds, there is some justification in referring to the slope of our curve as a measure of the acceptor activity of the phenol.

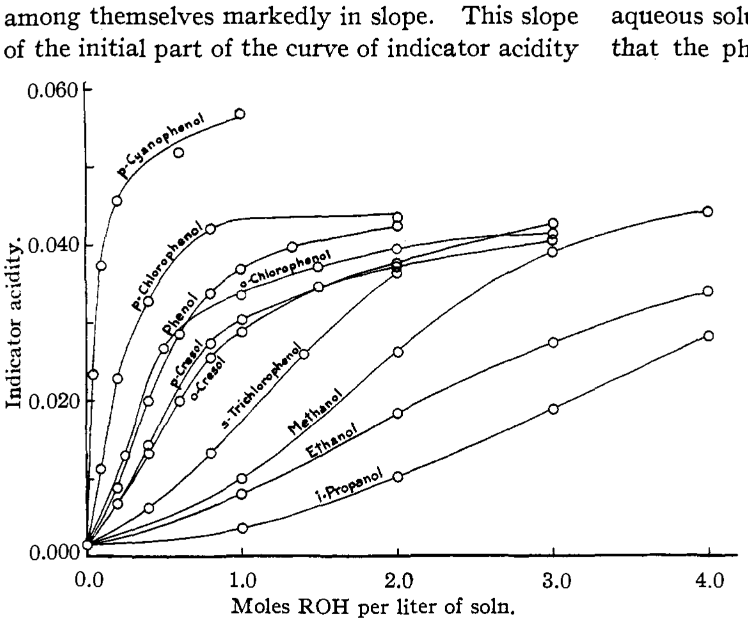

Fig. 2.

In many instances the logarithms of the rate or equilibrium constants for two reactions shown by compounds containing the same series of radicals have been found to be linearly related.[8] Although we have no equilibrium constant for a reaction involving the phenols as acceptors, it is of interest to plot the logarithm of the slope, our measure of acceptor activity, against the logarithm of the acid dissociation constant of the same phenol. Figure 3 shows such a plot including points for all the hydroxyl compounds measured. The acid dissociation constants taken are those recorded for aqueous solutions.[9] It is not too much to expect that the phenols will fall in the same order of acid strength in dioxane as in water, in view of the fact that acids *of the same type* have been found to have the same order of acidity in solvents of quite different character.[10]

All the phenols measured except *o*-chlorophenol and 2,4,6-trichlorophenol yield points which fall on a straight line in the figure. These chlorophenols deviate largely from the linear relationship, especially the symmetrical trichlorophenol, which has a K_a of 2.6 × 10^{-8}, the highest of the series, but is definitely the weakest acceptor of the group. The mere fact that these ortho-substituted phenols are known to have intramolecular hydrogen bonds[11] is not sufficient to explain why the acceptor activity should suffer in comparison to the acid strength, for if free rotation of the hydroxyl group were possible any restraint against

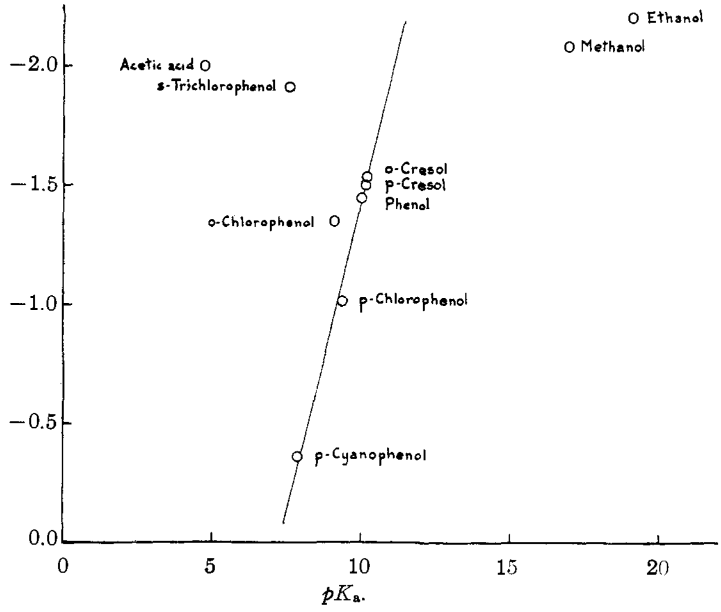

Fig. 3.

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[8] See Hammett, *Chem. Rev.*, **16**, 67 (1935); **17**, 125 (1935).

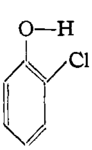
[9] Scudder, "Conductivities and Ionization Constants of Organic Compounds," D. Van Nostrand Co., New York, N. Y., 1914; Lucas, "Organic Chemistry," American Book Co., New York, N. Y., 1935; Boyd, *J. Chem. Soc.*, 1540 (1915).

[10] See, for example, Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

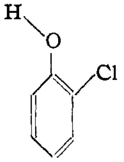
[11] Huggins, *J. Org. Chem.*, **1**, 407 (1937); Sidgwick and Callow, *J. Chem. Soc.*, **125**, 527 (1924).

the formation of an outside hydrogen bond (limitation of acceptor activity) would be attended by an equal restraint against the complete donation of the proton to an outside base (acid activity). What needs to be explained is a *selective* operation of the ortho-effect against the acceptor activity of the phenol.

An attractive explanation is to be found based upon Pauling's interpretation[12] of the infrared absorption spectra of the chlorophenols.[13] The evidence is that *o*-chlorophenol exists as an equilibrium mixture of the two spectroscopically distinguishable forms, I and II



I



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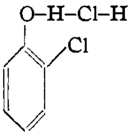

III

without detectable amounts of forms resulting from random rotation of the hydroxyl group about the C–O bond. The possibility of forming a hydrogen bond in the "*cis*" form, I, results in its predominance (estimated as 10 to 1) over the "*trans*" form, II, but the force restraining free rotation arises from the contribution of structures having carbon–oxygen double bond character, and hence requiring the hydroxyl group to lie in the plane of the ring. There is presumably no hindrance to acceptor activity in the *trans*-form. In the *cis*-form the breaking of the intramolecular hydrogen bond and forming of one outside results in a congested structure, III, for it amounts to placing the outside donor, in this case chlorine, on an extension of the O—H bond contiguous to the aromatically bound chlorine atom. We must suppose that this makes the formation of such a hydrogen bond less probable but not impossible. Trichlorophenol, which can have no "*trans*" form, still shows an acceptor activity about one-third as great as that of phenol, and one-fortieth of that to be predicted from its acid dissociation constant. *o*-Cresol, in which for obvious reasons the *trans*-form would be expected to predominate over the *cis*-, shows normal acceptor activity in terms of its acid strength.

Now, in the transfer of a proton to another base, the reaction whose equilibrium constant expresses the acidity of the phenol, a phenol must form a *transition state* resembling the phenol–hydrogen chloride complex, in its chemical and geometrical nature. In the case of the *o*-chlorophenols this transition state, too, would be hindered. If the acid dissociation were something whose rate we could measure, we should expect to find this rate retarded according to our present hypothesis of the ortho-effect. However, this reaction in normal cases proceeds too fast to measure, and as long as the hindrance to the formation of the transition state is not absolute, the equilibria of proton-transfer will continue to be established. Since the transition state appears on either side of the equilibrium, *the equilibrium of proton transfer should be exempt from this particular kind of ortho-effect.* Rates of acid-catalyzed reactions should not be exempt, for here any hindrance to a transition state in proton transfer will show itself in a lowering of the rate.

The work of Farinacci and Hammett[14] on the solvolysis of benzhydryl chloride in alcohol–water mixtures, and the interpretation of the work of Olson and Halford and of W. Taylor[15] in its light, make it seem highly probable that water, and to a lesser extent, alcohols, can also form hydrogen bonds with the chloride ion and so facilitate its removal from organic combination. We investigated methyl, ethyl and isopropyl alcohols with the results shown in Fig. 2. Here the initial rise is slow and not perfectly linear. In evaluating the slope use was made of the first point, but this is open to criticism since we do not know that this represents the true limiting slope. The points for methyl and ethyl alcohols have been included in Fig. 3. Here the assignment of abscissas is made on the basis of existing data[16] on the self-ionization of the pure liquids. It is, of course, difficult to compare these acid dissociation constants with the others determined in water solution. According to Faurholt,[17] the ionization constant of methanol in water solution is $10^{-15.5}$ at 18°, or 1.5 pK units greater than the figure we have plotted. This assignment is made in the belief that it cannot be far enough in error to bring the alcohol points onto the phenol line, and this is of some interest. It means that the alcohols are, in proportion to their acid strengths, far better acceptors than the phenols.

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[12] Pauling, THIS JOURNAL, **58**, 94 (1936).

[13] Wulf and Liddel, *ibid.*, **57**, 1464 (1935).

[14] Farinacci and Hammett, *ibid.*, **59**, 2542 (1937).

[15] Olson and Halford, *ibid.*, **59**, 2644 (1937); see Watson, *Ann. Reports*, 215 (1938).

[16] Bjerrum, Unmack, and Zechmeister, *Kgl. Danske Videnskab. Selskab. Math. fys. Medd.*, **5**, No. 11, 34 (1925); Danner and Hildebrand, THIS JOURNAL, **44**, 2824 (1922).

[17] Faurholt, *Z. physik. Chem.*, **126**, 85 (1927).

Meerwein found that benzoic and other organic acids had the ability to increase the acidity of ether–hydrogen chloride solutions. Acetic acid under our conditions shows an acceptor activity similar to that of the alcohols. A comparison with the phenols on the basis of acid strength in water may be misleading since if the acetic acid exists as double molecules in dioxane, then it is not present as the same species whose acid strength has been determined.

The results of Farinacci and Hammett indicate that water is a stronger acceptor than alcohol. Unfortunately, we are unable to demonstrate this with our present system, since water is a component of the indicator-equilibrium. The curve obtained with water is shown in Fig. 4. Its curious shape, which has been repeatedly checked, suggests a superposition of various effects. Among these we might expect to find the acceptor activity of water, its participation in the indicator-equilibrium, its basicity, and the fact that the addition of any quantity of it to dioxane multiplies the dielectric constant of the solution and accordingly greatly alters the state of ions in solution. The first and last of these effects might operate to give the curve a positive slope, while the two other effects would tend to make the curve descend as it does.

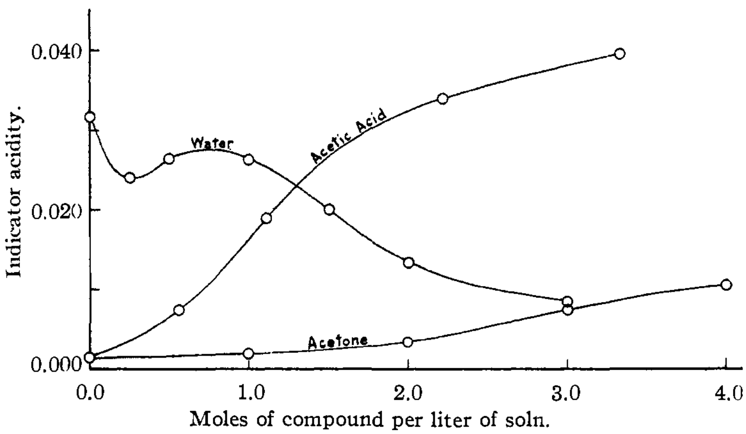

Fig. 4.

The carbonyl group has been demonstrated to have both donor and acceptor activity, arising out of its dipolar character. Toward the cyanide ion it functions as a pure acceptor,[18] while strong acids bring out its donor activity. In general, the reagent employed determines which type of activity will be displayed. Toward hydrogen chloride in dioxane the behavior of acetone is that of a feeble acceptor whose effect (Fig. 4) is so slight that it may be purely a solvent effect. Gordy[19] has presented data which indicate that acetone and dioxane are bases of about the same strength.

Several of the properties of dioxane as a solvent are worthy of comment for the way in which they determine the behavior of our system. In the first place, the basic strength of dioxane is sufficient to assure us that the hydrogen chloride occurs entirely chemically combined with the solvent, as dioxanonium chloride. This same basicity of dioxane causes phenol to be largely combined with the dioxane in which it is dissolved and not associated, as it would be in non-basic solvents of low dielectric constant.[20] When we speak of the phenols as if they were free, we refer to a small fraction which must be free in order to have acceptor activity, since there is no evidence that hydrogen can be attached to more than two other atoms at once.

The conductivity data of Chesterman[21] and Mounajed[22] show that in solutions of hydrogen chloride in ether the diethyloxonium chloride is only slightly dissociated into free ions. The dielectric constant of dioxane is still less (2.2) than that of ether (4.6) so that in our present system we may expect a great deal of ion association, not only into pairs but into clumps of greater size.[23]

The well-known "leveling" effect of a basic solvent, that of converting into its own conjugate acid all stronger acids which might be formed in solution, is important in bringing out the effects which we have observed. In a completely non-basic solvent, alcohols are known to behave as bases toward hydrogen chloride, and this effect, if present here, would completely conceal the acceptor properties of the alcohols. These acceptor properties appear here because there is practically no hydrogen chloride present, but only the much

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[18] Lapworth, *J. Chem. Soc.*, **83**, 995 (1903).

[19] Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[20] Meisenheimer and Dormer, *Ann.*, **482**, 130 (1930); M. and R. Freymann, *Bull. soc. chim.*, [5] **4**, 944 (1937); Belluci and Grassi, *Gazz. chim. ital.*, **43**, 712 (1913); Morgan and Pettet, *J. Soc. Chem. Ind.*, **54**, 22 (1935).

[21] Chesterman, *J. Chem. Soc.*, 906 (1935).

[22] Mounajed, *Compt. rend.*, **197**, 44 (1933).

[23] Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933); Kraus and Vingee, *ibid.*, **56**, 511 (1934).

weaker acid, dioxanonium chloride, from which methyl or ethyl alcohol is incapable of taking a proton.[19] Hence the acceptor properties of the alcohols are not overlaid. If these experiments were carried out in benzene, it would surely be impossible to detect the acceptor properties of the alcohols or of acetone, and we might even find phenols displaying basic character.

It is equally obvious that if any base is to be used as solvent which, like dioxane, combines completely with hydrogen chloride, the solvent must not be one which allows complete ionization of the resulting salt. Such ionization would mean that the maximum acidity of which the system was capable was already reached, and complex-formation by the acceptors would not be detectable by the indicator method.

It is of interest that the acceptor properties of phenol have been utilized[24] in promoting the elimination of hydrogen bromide from 9,10-dibromo-9,10-dihydroanthracene.

Experimental

Apparatus.—A Bausch and Lomb colorimeter (No. 2504) of the Dubosque type was used. Water-jacketed all-glass cups were clamped firmly in place and provided with machined brass caps with felt linings which fitted the plungers and minimized the entrance of moisture from the air. Water at 25.00 ± 0.05° from a thermostat was circulated through the jackets.

1,4-Dioxane.—The technical product was purified by refluxing for eight to fifteen hours with concentrated hydrochloric acid to destroy acetals, drying, refluxing with sodium until no reaction occurred, and distilling. The fraction used boiled at 101.1–101.3° and melted at 11.8°.[25] It was stored in a nitrogen atmosphere over sodium wire in a bottle closed with a paraffin-treated cork.

***p*-Dimethylaminoazobenzene** from the Eastman Kodak Co. was recrystallized three times from ethyl alcohol and carefully dried before use. It melted at 115–116°.

2,2′,2″,4,4′-Pentamethoxytriphenylcarbinol was prepared by the method of Lund.[26] Several recrystallizations from hot ethanol gave well formed white crystals of m. p. 145.5–146.5°.

Phenols.—With the exception of *p*-cyanophenol the phenols were prepared by the fractional distillation of good commercial grades. The *p*-cyanophenol[27] was synthesized and purified by crystallization from hot water and melted at 111.5–112.5° after careful drying. To obtain *p*-chlorophenol free from hydrogen chloride it was necessary to extract it with water, dry, and distil under diminished pressure. The fraction used boiled at 119.2–119.7° under 27 mm. pressure. The *o*-cresol boiled at 105.9–106.0° under 50 mm. pressure. The other phenols were fractionally distilled at atmospheric pressure. The phenol melted at 40.6° and boiled at 178.0–178.4°. The *p*-cresol boiled at 202.4–202.5° at atmospheric pressure. The *o*-chlorophenol boiled at 174.8–174.9° at 756 mm. The *sym*-trichlorophenol melted at 66.5–67.5°. All the phenols were stored in an atmosphere of nitrogen.

Methanol.—A commercially available "acetone-free" product was refluxed with sodium hydroxide and iodine, distilled, dried by refluxing with magnesium and a little iodine, and finally distilled. It gave no precipitate with aluminum ethoxide.

Ethanol (absolute, from the Commercial Solvents Co.) was refluxed with silver nitrate and potassium hydroxide for seven to eight hours, distilled, and finally dried by the magnesium method. It also gave a negative test with aluminum ethoxide.

Isopropanol was heated under reflux for thirty hours with its weight of quicklime and distilled. The middle fraction, which boiled at 82.2°, was used.

Acetone (alcohol-free) was refluxed with potassium permanganate and a little sodium hydroxide for a few hours and distilled. The middle fraction of the distillate was shaken with freshly dried potassium carbonate for about twelve hours. The product distilled at 56.2°.

Acetic acid, provided by Rolf Altschul, had been heated with chromic anhydride and a little acetic anhydride and distilled through a six-foot (1.8-meter) packed column. The fraction used boiled at 118.3° at 764 mm. and had a freezing point of 16.6° just before use.

Summary

Seven phenols and three alcohols have been investigated and all found to increase the acid strength (measured by an indicator) of solutions of hydrogen chloride in dioxane. This is interpreted as due to the formation of a hydrogen bond with the chlorine atom of the hydrogen chloride by the hydroxyl group of the phenol or alcohol. A composite quantitative measure of this effect is had from colorimetric determinations. The hydrogen bond formation appears to run parallel to the acid strength in the series of phenols except for phenols with ortho-substituents capable of intramolecular hydrogen bonding, which are far less efficient "acceptors" than would be expected from their acid strength. This deviation is regarded as an argument against the diversion of the term "acidity" to cover activity as an electron acceptor.

This property of hydroxyl compounds is correlated with the mechanisms of the Wagner–Meerwein rearrangement and the solvolysis of secondary and tertiary halides. Measurements on acetic acid and acetone are included for comparison.

CAMBRIDGE, MASSACHUSETTS

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[24] Barnett and Cook, *J. Chem. Soc.*, 1084 (1924).

[25] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931); Scatchard and Benedict, THIS JOURNAL, **58**, 837 (1936); Hess and Frahm, *Ber.*, **71**, 2627 (1938).

[26] Lund, THIS JOURNAL, **49**, 1346 (1927).

[27] Ahrens, *Ber.*, **20**, 2953 (1887).