cated in the table. The recovery of ethyl chlorocarbonate as well as the amount of 1-carbethoxypyrrole obtained, indicate that 1.75 mole each of the Grignard reagent and the ethyl chlorocarbonate per mole of pyrrole would give as good a yield as did the proportion of reactants used above.

Table I

Products of Reaction

Fraction	Compound	Boiling range, °C.	Weight, g.	Yield, %
1	Ethyl chlorocarbonate	Up to 55° (65 mm.)	10	..
2	1-Carbethoxypyrrole	60– 65° (7 mm.)	9.2	26.4
3	2-Carbethoxypyrrole	100–110° (7 mm.)	0.5	1.5
4	1,2-Dicarbethoxypyrrole	125–135° (7 mm.)	34.2	65.0
	Residue		1.8	
			Total	92.9

The fourth fraction was found to be nearly pure 1,2-dicarbethoxypyrrole[5] since on refractionation 98% of the material distilled at 132–134° at 8 mm. The 1-carbethoxypyrrole had a b. p. of 57–58° at 7 mm., and 178–180° at 740 mm., and d^{25} 1.037, n^{25}_{D} 1.4698. The boiling point of this compound checks with that reported by other investigators. Only one author has reported the density and refractive index of this compound and these values do not check with those given above. However, the compound seems to be sufficiently characterized by the fact that it takes up 4 atoms of hydrogen to give a non-basic compound having the correct analysis for a carbethoxypyrrolidine, indicating that the carbethoxy group is on the nitrogen atom. The 1-carbethoxypyrrole is better prepared from potassium pyrrole and ethyl chlorocarbonate.[7a,9]

The 2-carbethoxypyrrole had a m. p. of 41–42° when crystallized from low-boiling petroleum ether and a b. p. of 102–104° at 7 mm.

The 1,2-dicarbethoxypyrrole so obtained was hydrogenated rapidly and quantitatively over Raney nickel.[5] In a typical experiment 1,2-dicarbethoxypyrrolidine b. p. 133–134° (8 mm.) was obtained in 98% yield by the hydrogenation of 0.2 mole of the pyrrole ester over 5 g. of Raney nickel under 100 to 200 atm. of hydrogen at 50 to 85° in less than one hour.

The 1,2-dicarbethoxypyrrolidine (10.6 g. or 0.05 mole), was refluxed with 25 cc. of concentrated hydrochloric acid for three hours; 10 cc. more of hydrochloric acid was then added and the refluxing continued for two hours. The mixture was then evaporated on a steam-bath. The partially crystallized residue was dissolved in 100 cc. of water and treated with 0.10 mole of freshly precipitated silver carbonate. After filtration, the filtrate was treated with hydrogen sulfide. The solution was heated with 1 g. of activated charcoal and this together with the silver sulfide was removed by filtration. Upon evaporation of the filtrate on a steam-bath, there was obtained 5.7 g. of a gummy crystalline mass. This was dissolved in 25 cc. of hot ethanol and 50 cc. of hot dioxane was added. After cooling the solution with ice, the crystalline proline was filtered off and dried in a desiccator. The yield was 5.2 g. (90%), m. p. 204°. The picrate was prepared by dissolving 1 g. of proline and 2 g. of picric acid in 2 cc. of hot acetic acid, followed by addition of 7 cc. of ether and cooling. The picrate was recrystallized from ethanol and showed a m. p. of 136°.

Summary

Crystalline *dl*-proline may be prepared in yields of 55 to 60% from pyrrole through the intermediate formation of 1,2-dicarbethoxypyrrole and 1,2-dicarbethoxypyrrolidine. A method for the synthesis of 1,2-dicarbethoxypyrrole has been devised and developed.

Madison, Wisconsin Received March 13, 1936

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[9] Ciamician and Dennstedt, *Ber.*, **15**, 2579 (1882); *Ber.*, **60**, 196 (1927).

[Contribution from the Converse Memorial Laboratory of Harvard University]

A Further Study of Extremely Weak Acids

By W. K. McEwen

The purpose of this paper is to report the new methods used and the results obtained in the study of extremely weak acids.

It has been shown by Conant and Wheland[1] that reactions of the type

$$R_1H + R_2^- \rightleftharpoons R_1^- + R_2H$$

may be used to determine the relative acid strength of very weak acids such as the aromatic and aliphatic derivatives of water, ammonia and methane. The determination of the relative amounts of the different substances present at the point of equilibrium is a measure of the relative strength of the two acids. This can be determined in either of two ways.

The first method used was to observe the change in color. Since many compounds of the type R^- are colored, it is only necessary to mix the reactants and observe whether or not a change in color results. As a check the products of the reaction are also mixed. From such observations the compounds can be arranged in a series of de-

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[1] Conant and Wheland, This Journal, **54**, 1212 (1932).

creasing acid strength. Using equivalent quantities, and assuming that apparent complete reaction corresponds to at least 90% reaction, a minimum difference in *pK* for the acids may be taken as 2 *pK* units.

A second method used by Conant and Wheland was to introduce carbon dioxide into the equilibrium mixture, isolate the acids and from their analysis draw similar conclusions regarding the equilibrium and the relative strengths of the acids.

Three methods have been used in the present paper to extend the series of weak acids.

I. Colorimetric Method

Essentially the same method as devised by Conant and Wheland was used to measure acids having colored sodium or potassium salts. Twenty-five acids were investigated by this method. These results, with the results of the two following methods, are summarized in Table II.

Each compound that has a colorless metallic salt was measured against the nearest colored compound appearing in the table, and was found to differ from it in acidity by at least 2 *pK* units. Every compound having a colored metallic salt was measured against as many compounds as necessary to determine its position in the table. However, alpha-naphthylfluorene could not be measured against phenylfluorene as the metallic salts of both compounds have approximately the same color. For this same reason, phenylxanthane could not be measured against xanthane. The last four compounds in Table II had been measured by Conant and Wheland using a five-fold quantity of the hydrocarbon, so that they were found to differ by only a minimum of 0.4 *pK* unit. By using equivalent quantities, the minimum difference was extended. It was found that etioporphyrin I[2] had an acidity approximately that of the alcohols. The formation of the sodium salt of the porphyrin is accompanied by a striking spectroscopic change. Etioporphyrin I forms a disodium salt[3,4] but no difference in acidity could be found between its first and second dissociation constant.

Other compounds were measured colorimetrically but the data obtained were insufficient to warrant placing them definitely in Table II. Diethylcarbinol, diphenyl-alpha-naphthylcarbinol, phenylxanthydrol, acetanilide, tricarbomethoxymethane, 2,4-dimethylpyrrole and pyrrole were found to be 2 *pK* units stronger than phenylfluorene, while tertiary butylfluorene seemed to be weaker than triphenylmethane.

II. Spectroscopic Method

This method is strictly analogous to the ordinary water system of acid–base titration. That is, the acid to be measured is titrated with sodium triphenylmethyl, a strong base, in the presence of a minute amount of etioporphyrin I as an indicator, in an inert atmosphere. The change in the indicator is apparent when the shift in the absorption bands is observed with a small hand spectroscope. If the porphyrin is at least 2 *pK* units stronger than the acid, it will take the sodium from the first few drops of sodium triphenylmethyl. Likewise, if both the acid and the porphyrin are the same strength, the porphyrin will be partially converted into its basic form at the start, but will not be completely converted until the end of the titration. The results of this method are also summarized in Table II. This method was useful in showing that of the alcohols measured, all were at least 2 *pK* units weaker than etioporphyrin except methyl alcohol which has an acidity very close to that of etioporphyrin. Standard pyrrole (2,4-dimethyl-3,5-dicarbethoxypyrrole) was only slightly weaker. Experiments with other porphyrins and porphyrin-like compounds showed that they were at least 2 *pK* units stronger than etioporphyrin I. However, N-methyletioporphyrin I[4] is only about 1 *pK* unit stronger than etioporphyrin itself. This compound is interesting in that one of the imino hydrogens of the porphyrin ring is replaced with a methyl group, making the compound a monobasic acid. According to Hammett and Deyrup,[5] it is thus better suited for an indicator.

III. Polarimetric Method

The third method is useful in dealing with colorless compounds and permits in some cases more exact values for the relative acid strength of the compounds studied. In this method an optically active acid is used and the position of equilibrium determined with the aid of a polarimeter. The optical activity of the equilibrium mixture together with the values for the optical activity of the acid and salt allow one to calculate

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[2] Fischer, Baumann and Riedl, *Ann.*, **475**, 205 (1929).

[3] Fischer and Neumann, *ibid.*, **494**, 225 (1932).

[4] Work to be published.

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

TABLE I

Acid	Cc. of soln.	Total concn. moles/liter	Menthylate, %	Moles of acid	α	*pK*
CH_3OH	43	0.119	27	0.0002	−1.41	−1.0 (min.)
	43	.119	27	.0004	−1.44	−0.2 (min.)
$(C_6H_5)CH_2OH$	10	.100	95.3	.000385	−1.40	−1.4
	34.1	.119	9			
$(C_6H_5)_2CHOH$	43	.071	88	.00286	−0.84	−0.86
	43	.071	88	.00298	− .86	− .92
	30	.100	95.3		− .80	− .86
	(14			.215 *M* C_6H_6 soln.)		
	43.6	.119	27	.0006	−1.47	−1.2
$(CH_3)_2CHOH$	10	.100	95.3	.00092	−1.47	−1.1 (max.)
	33.4	.119	9			
	43.1	.119	27	.00053	−1.45	−0.9
	43.1	.119	27	.00053	−1.44	− .7
$(CH_3)_3COH$	17.5	.100	95.3	.0010	−0.36	− .31
	25.3 C_6H_6					
	18.5	.100	95.3	.0010	− .38	− .43
	24.6 C_6H_6					
$(C_2H_5)(CH_3)_2COH$	23.9	.100	95.3	.00203	− .50	+ .12
	19.3 C_6H_6					
	24.4	.100	95.3	.00184	− .51	− .12
	19.3 C_6H_6					
$(C_6H_5)COCH_3$	43.6	.119	27	.0006	−1.39	+ .2
Phenylfluorene	43	.100	95.3	.00186	−0.53	+1.8 (max.)
	43	.100	95.3	.00130	− .54	+1.5 (max.)

$[\alpha]^{23}_{D}$ sodium *l*-menthylate −12.2°. $[\alpha]^{23}_{D}$ *l*-menthol −45.6°.

the extent to which the reaction has gone. Thus, if a weak acid is allowed to react with sodium menthylate,[6,7] the amount of free menthol produced can be measured and the strength of the weak acid, relative to menthol, can be calculated. This was done with six alcohols, one enol and one hydrocarbon. The data are shown in Table I.

It should be noted that the *pK* values, given in the table above, are relative to menthol, a negative value indicating that an acid is stronger than menthol. A precipitate formed in the reaction with those acids whose value is followed by the abbreviation "max." The consequent shift in the point of equilibrium results in a maximum value. That is, the acid is no stronger than the value given, and may be weaker. In attempting to measure the acidity of methyl alcohol, it was found that the reaction went substantially to completion with the formation of a precipitate. It was then necessary to determine the solubility of sodium methylate in benzene in order to obtain the *minimum* value given in the table above. The order of magnitude of the solubility was necessary, rather than its precise value.

There are too few alcohols from which to draw definite conclusions, but it is apparent that the acidities fall into three groups corresponding to the primary, secondary and tertiary structures of the alcohols, with the acidity decreasing in that order. Evidently the determining factor in the acid strength of the alcohols resides in the functional group being of primary, secondary or tertiary character, and the substituents whether aliphatic or aromatic are of secondary influence.

From the position of acetophenone in the table, one can make a rough calculation of the fraction of the material which is present as enol. This is so small as not to be measurable by analytical means. The structure of the enolic form (a double bond alpha-beta to an hydroxyl group) is similar to phenol, and should have an approximate *pK* value of 10. This is probably fairly close, as the value for ethylacetoacetic ester has been found to be 12. Assuming the *pK* value of the pure enolic form of acetophenone is 10, the equilib-

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(6) F. H. Yorston of the Forest Products Laboratories of Canada stated that "I obtained a definite though small positive rotation in a toluene solution of the laevo alcohol [octenol-2] on adding potassium." (Private communication to J. B. Conant.)

(7) Professor E. P. Kohler suggested optically active menthol.

rium constant for the reaction keto $\rightleftarrows$ enol would have to be 10^{-9}.

IV. Summary

In order to relate all the acids, it is necessary to choose some arbitrary standard to which to relate them. The standard chosen in this work is methyl alcohol whose acidic dissociation constant has been measured accurately by A. Unmack[8] and found to be 10^{-16}, giving it therefore a *pK* value of 16.

Since the values obtained by the three methods are transferred directly to Table II with no correction for solvent effects, or for changes of solvent or of concentration, the values should be considered as accurate to about one power of ten.

TABLE II

pK	Compound	Method used		
14–15	N-Methyletioporphyrin[1]		s[2]	
16	Etioporphyrin I		s	
16	Methyl alcohol (standard)	c	s	p
16.5	Standard pyrrole	c	s	
18[3]	Benzyl alcohol	c	s	p
	Ethyl alcohol	c	s	
	Benzhydrol	c	s	p
	Isopropyl alcohol	c		p
19	Triphenylcarbinol	c	s	
	Tertiary butyl alcohol	c		p
	Tertiary amyl alcohol	c	s	p
	Menthol			p
	Acetophenone	c	s	p
21	*Phenylfluorene* (C)	c		p
	α-Naphthylfluorene (C)	c		
	Phenylacetylene			
	Indene (C)			
23	Diphenylamine[4]	c		
25	*Fluorene* (C)	c		
27	Aniline[5]	c		
	p-Toluidine	c		
	p-Anisidine	c		
29	*Xanthane* (C)	c		
	Phenylxanthane (C)	c		
31	*Diphenylbiphenylmethane* (C)	c		
33	*Triphenylmethane* (C)	c		
34	*Diphenyl-alpha-naphthylmethane* (C)			
35	*Diphenylmethane* (C)	c		
36	*Diphenylmethylethylene* (C)			
37	*Cumene* (C)	c		

Compounds italicized appeared in the table of Conant and Wheland.

(C) = compounds having colored metallic salts
s = measured spectroscopically, using etioporphyrin as an indicator
c = measured colorimetrically
p = measured polarimetrically
1 = work to be published concerning this compound
2 = measured spectroscopically against methyl alcohol
3 = *pK* values 18–37 are minimum *pK* values
4 = equilibrium approached from both ends when measuring against fluorene and phenylfluorene
5 = acidity determined by Conant and Wheland, but not included in their table

Where feasible compounds were measured by two or more methods in order to check their positions in the table.

The author wishes to express his gratitude and appreciation to both former Professor James Bryant Conant who directed the research on the colorimetric and spectroscopic methods and Professor Henry Edward Bent who directed the research on the polarimetric method.

Experimental Part

Treatment of Compounds.—All liquid alcohols were carefully fractionated from their sodium salts and kept in sealed bottles in a desiccator over phosphorus pentoxide. Different samples of the same alcohol were used in various runs to guard against any one sample being contaminated.

The liquid amines were distilled from potassium hydroxide and kept in sealed bottles in a desiccator over potassium hydroxide.

All solids were recrystallized until pure by melting point and other tests, and dried in a drying pistol.

The nitrogen was passed through Fieser's solution, lead acetate solution, sulfuric acid, phosphorus pentoxide towers and finally through a xylene solution of sodium benzophenone ketyl. When a piece of apparatus is filled with nitrogen, it is done so by evacuating with an oil pump and then filling with nitrogen, the apparatus being flamed over with a micro-burner during the process. This procedure is carried out three times. The apparatus is of course allowed to cool before a solution is added so as not to evaporate any solvent. When the apparatus is cleaned, cleaning solution, soap and water, distilled water, alcohol, ether and dry, distilled ether are used in the order named.

Colorimetric Method.—The storage flask for the metal-alkyl solution was similar to that used by Conant and Wheland[1] for the storage of their metal-alkyl solutions, except that a calibrated Pyrex buret of 25-cc. capacity was used in place of the roughly calibrated side-arm, and two slant-bore stopcocks in series were used instead of the mercury seal stopcock. The lower stopcock bears the brunt of the frequent evacuations and fillings of the reaction flask, and thus protects the upper stopcock. As there is little or no difference in pressure on either side of it, there is no tendency for the ether to make channelings in the ether-soluble grease. The lower stopcock can be regreased, without danger of changing the titer of the solution, if the key is only taken from the socket when there is a strong positive pressure of nitrogen so as to prevent back diffusion. The upper stopcock need only be regreased at very infrequent intervals, and this is done in the same manner as the lower stopcock, except that the solution is again standardized to be sure that there has been no change.

A different reaction flask was developed. This was a small flask of 100 cc. capacity which was joined to the

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(8) A. Unmack, *Z. physik. Chem.*, **133**, 45 (1928).

lower terminal of the stopcocks on the storage flask by means of a ground glass joint. The nitrogen train was also attached to this flask with a ground glass joint. The substance to be measured, if a solid, is weighed into a short length of glass tubing which is then capped on each end with two pieces of glass tubing sealed at one end and fitting smoothly over the tube, forming a capsule. This capsule is then placed in a short length of 15-mm. tubing bent at an angle of 45°, sealed off at one end and carrying at the other end a 15-mm. male standard taper ground glass joint, which in turn fits into the female joint attached to the reaction flask. The tube containing the capsule is turned downward while the system is being filled with nitrogen. To introduce the compound, the tube is rotated, allowing the capsule to descend. Usually the capsule slips apart on hitting the bottom of the flask, but if this does not happen the apparatus is either gently shaken to break it open, or the capsule is covered with a layer of solution, and a vacuum is applied. The gas inside the capsule bursts it apart on expanding. The compound may then be measured directly against the metal-alkyl solution in the reservoir, by adding an equivalent amount and observing the color change. When the solution is standardized against benzoic acid, this method is used.

If the substance to be measured is a liquid, a somewhat different procedure is used. The entire apparatus is connected using, however, a little longer crooked tube. The system is evacuated and filled with nitrogen several times. The liquid is pipetted into one of the caps of the capsule, the crooked tube is disconnected from the apparatus, the cap is placed in it and it is filled with benzene, and reconnected to the reaction flask. The benzene is then frozen with a salt and ice mixture placed around the outside of the tube. When the benzene has frozen, the system is evacuated and again filled with nitrogen in order to get rid of any air that may have entered the apparatus when the crooked tube was temporarily removed. When it is desired to introduce the sample, the benzene is melted, the tube rotated and the contents run into the flask.

There was a certain amount of difficulty involved in the handling of volatile amines like *n*-butylamine and di-*n*-butylamine. For this reason, an attempt was made to use the amine hydrochlorides, and to treat them with one equivalent of sodium triphenylmethyl in order to liberate the free amine directly in the reaction flask. The amine hydrochlorides were so insoluble in ether that the reaction took place too slowly and did not seem to go to completion within a reasonable length of time. Although aniline hydrochloride worked fairly satisfactorily, and gave the same results as with aniline itself, the method was abandoned as it was too slow with the other amines.

Tertiary Butylfluorene.—2.38 grams (0.01 mole) of tertiary butylfluorenol,[9] 10 cc. of glacial acetic acid, 2 cc. of hydrogen iodide (sp. gr. 1.7) and 1. g. of red phosphorus were refluxed for four hours in a 50-cc. Erlenmeyer flask under a return condenser. The solution was filtered while hot and water added to precipitate the hydrocarbon, which was slightly pinkish. It was recrystallized from methyl alcohol to a melting point of 98–99° and a yield of 1.6 g. (73%) of fine white needles that gave no color in sulfuric acid. This product was further dried in a drying pistol at 61°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.68; H, 8.11.

Spectroscopic Method.—When using this method, the same apparatus is used as in the colorimetric method. The acid to be measured and a few specks of etioporphyrin were frozen in benzene in the long crooked tube of the apparatus. When the flask is ready, the benzene is melted, providing a homogeneous solution on which the effect of the sodium triphenylmethyl readily may be determined by viewing the solution through a small hand spectroscope. As to the efficiency of the indicator, dilution experiments showed that the basic form in the presence of the acidic form could be detected if 50% or greater. The acidic form could be detected in the presence of its basic form in as low an amount as 10%. This range, 50–90%, compares favorably with the range of the usual color indicators.

Polarimetric Method.—The storage flask for the sodium menthylate solutions was the same as used in the other methods for the storage of metal-alkyl solutions. The polarimeter cell was made from approximately 21-mm. Pyrex tubing with Pyrex windows sealed on the ends, and a slant-bore stopcock sealed to the middle of the tube. The length of the cell was 1.995 dec., and it had a capacity of about 43 cc. There was little or no strain noticeable in the windows. This cell was connected to the storage flask by a ground glass joint. The nitrogen train was attached between the junction of the cell and the storage flask. All the ground glass joints were standard taper.

Experiments were tried with fusel oil as a possible alcohol for the polarimetric method, but the difficulty of separating the active component and the inadvisability of using a mixture made its usefulness doubtful.

Difficulties arose in the preparation of pure sodium menthylate. It had been found in previous work on the preparation of alcoholates that they often turned yellow This yellow coloration was thought to be due to side reactions caused by the relatively high reaction temperatures. To prevent this, 40% sodium amalgam was used instead of sodium wire, and the mixture of amalgam, alcohol and benzene was shaken at room temperature under nitrogen until no more hydrogen was given off. This procedure formed a colorless solution of sodium *l*-menthylate. However, if air is present, the yellow color develops. Benzene was used as a solvent because it would dissolve sodium *l*-menthylate at least up to concentrations of 0.1 mole per liter. The sodium *l*-menthylate appeared very insoluble in ether. All polarimetric reactions were carried out using benzene (dried over sodium) as the solvent, under an atmosphere of dry, oxygen-free nitrogen. The polarimeter was readable to 0.01°. The light source was a General Electric sodium vapor lamp. The light from this lamp was about 99% monochromatic, by spectroscopic examination.

In order to obtain the specific rotation of pure sodium *l*-menthylate, the solution of menthylate, obtained by shaking with 40% sodium amalgam, was titrated with sodium triphenylmethyl just until the formation of a permanent end-point. The reaction between *l*-menthol and 40% sodium amalgam did not go to completion, so to be sure that all the *l*-menthol was finally converted to sodium

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(9) H. W. Scherp, "Rate of Autoxidation of Di-aryl-di-fluoryls," Thesis, Harvard University, 1931, p. 105.

l-menthylate, it was titrated with sodium triphenylmethyl. This solution was then measured in the polarimeter and the specific rotation for sodium *l*-menthylate was found to be $[\alpha]^{23}_{\mathrm{D}}$ −12.2 ± 0.6. Patterson and Taylor[10] give the specific rotation of menthol as $[\alpha]^{23}_{\mathrm{D}}$ −45.57.

An ethereal solution of menthol was successively diluted from 1 to 0.0125 *M*, and no change was observable in the specific rotation.

Patterson and Taylor[10] have shown that *l*-menthol in benzene is "practically insensitive to temperature change." With the menthylate solution, a 0.003° change in rotation was observed for every degree change in temperature. In the same way, the temperature effect on the equilibrium of a reaction is from 0.001 to 0.003° change in rotation per degree temperature change. Since the polarimetric room was thermostatted to 24.5 ± 1.5°, the maximum change in rotation due to temperature change is less than the experimental error.

Since the specific rotation of both pure menthylate and menthol is known, it is only necessary to know, in a given solution, the total concentration of menthol, either as menthol or menthylate, and a measurement of the rotation gives the concentrations of both. The total concentration was found by weighing the amount of pure menthol used and measuring the benzene volumetrically.

The rates of these metathetical reactions were all practically instantaneous. In the measurement of benzhydrol, three to five minutes after adding the benzhydrol, the reaction had reached a value that did not change after one and one-half hours. A second reading after at least one-half hour had elapsed was taken on tertiary amyl alcohol, tertiary butyl alcohol, isopropyl alcohol and acetophenone, and no change was observed. Of the remaining compounds, precipitates appeared with methyl alcohol and phenylfluorene which took quite a while to settle (one to two hours) and only on benzyl alcohol was no second reading taken after some time had elapsed. So with no alcohol was a shift in the rotation observed. The rate of the reaction was faster than could be detected.

Since most of the sodium salts of the alcohols are fairly insoluble in benzene, it was necessary to prevent their formation as much as possible. This was done by using smaller and smaller amounts of alcohol and menthylate and larger and larger quantities of menthol, until no precipitate formed. This was not always successful, and the accuracy of the readings was reduced. When the menthol was used in solution to partially block the reaction, a small amount of menthylate was also present in the solution in order to be sure that there was no contaminating substance present.

Solubility of Sodium Methylate in Benzene.—A 100-cc. flask was filled with benzene under nitrogen and a large amount of sodium wire was added. One-half cc. of methyl alcohol was added against a current of nitrogen. A rapid reaction occurred. The flask was left for two days, after which three samples were removed and titrated with 0.01 *N* hydrochloric acid, using phenolphthalein as an indicator. The value for the solubility was found to be 0.3 to 0.9 of a millimole per liter. A correction was then made for the dissolved sodium hydroxide. The solubility was determined by sealing sodium hydroxide, sodium and benzene in a small flask and shaking overnight. The solution was titrated and found to contain 0.1 millimole of sodium hydroxide per liter of benzene.

Summary

1. Fifteen weak acids have been measured colorimetrically and inserted in a table of acids of decreasing strength. Eight other weak acids have been investigated by this method.

2. Ten weak acids have been measured spectroscopically by an indicator method that is described.

3. The acidity of six alcohols, one enol and one hydrocarbon have been determined by a polarimetric method that is described.

Cambridge, Mass. Received February 25, 1936

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(10) Patterson and Taylor, *J. Chem. Soc.*, **87**, 122 (1905).

[Contribution from the Department of Chemistry, McGill University]

The Diffraction of X-Rays by the Higher Polyethylene Glycols and by Polymerized Ethylene Oxides[1]

By W. H. Barnes and Sydney Ross

In recent studies[2] Hibbert, Perry and Pullman have obtained very strong evidence in support of the suggestion[3] that polymerized ethylene oxides probably have the same composition as the polyethylene glycols (*i. e.*, $HOCH_2CH_2(OCH_2CH_2)_xOCH_2CH_2OH$). Since the former already have been subjected to x-ray examination,[4] and since specimens of polymerized ethylene oxides and polyethylene glycols of comparable molecular weights[5] were available, an opportunity was presented for a comparison of the diffraction

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(1) This paper constitutes No. LI in the series of "Studies on Reactions Relating to Carbohydrates and Polysaccharides," by Dr. Harold Hibbert and co-workers.

(2) Hibbert and Perry, *Can. J. Research*, **8**, 102 (1933); Perry and Hibbert, *ibid.*, **B14**, 77 (1936). The method of preparation, the constitution and the physical and chemical properties of the higher polyethylene glycols and polymerized ethylene oxides will be discussed in forthcoming articles by Pullman and Hibbert.

(3) (a) Staudinger and Schweitzer, *Ber.*, **62**, 2395 (1929); (b) Carothers, *Chem. Rev.*, **8**, 391 (1931); (c) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932, p. 287.

(4) Sauter, *Z. physik. Chem.*, **B21**, 161–185 (1933).

(5) Molecular weights stated throughout this paper refer to values in solution as determined by Staudinger's viscosity methods,[3c] p. 56 *et seq.*