
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 62

JANUARY 10, 1940

NUMBER 1

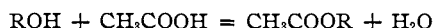
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Analytical Procedures Employing Karl Fischer Reagent.¹ II. The Determination of Alcoholic Hydroxyl

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Alcoholic hydroxyl is usually determined acidimetrically by means of acetyl chloride and pyridine² or by one of the several acetic anhydride procedures. These methods, however, are lacking in sensitivity where the sample contains considerable amounts of water or acids. Water, for example, reacts mole for mole with acetyl chloride, in competition with alcohols, and necessitates the use of smaller analytical samples in order to maintain the necessary excess of reagent.

In the present research a titrimetric procedure for hydroxyl independent of acidimetry has been developed. This new procedure is useful over a wide range of compositions and is remarkably precise in the presence of large amounts of water or acids. The analysis depends upon the general reaction



according to which one mole of water is liberated for each equivalent of hydroxyl esterified. By employing a large excess of acetic acid and making use of boron fluoride as an esterification catalyst,³ it is possible to shift the equilibrium almost completely in favor of water and ester. A measure of the water formed is obtained by direct titration with Karl Fischer reagent.

(1) This reagent, discussed in detail in the first paper of the series [Smith, Bryant and Mitchell, *THIS JOURNAL*, **61**, 2407 (1939)], consists of a solution of iodine, sulfur dioxide and pyridine in methanol. It is specific for water.

(2) Smith and Bryant, *THIS JOURNAL*, **57**, 61 (1935). References covering the acetic anhydride procedures are included.

(3) (a) Bowlus and Nieuwland, *ibid.*, **53**, 3837 (1931); (b) Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932); (c) Hennon, Hinton and Nieuwland, *ibid.*, **55**, 2857 (1933).

The new hydroxyl procedure is applicable to aliphatic and alicyclic alcohols in general, including branched chain types and hydroxy acids, also such aromatic alcohols as have the hydroxyl group attached to an aliphatic side chain. Phenols, however, do not react completely. Some unsaturated terpene alcohols, on the other hand, give results greater than the theoretical.

Differences in the relative esterification rates of aliphatic and strictly aromatic alcohols (*i. e.*, phenols) have made possible a method for differentiating these two classes of compounds. Under the proper conditions aliphatic alcohols are esterified or dehydrated⁴ almost completely, while phenols react only to a very small extent. The selective action observed here is probably due as much to differences in the equilibrium constants of the two series, as to purely kinetic differences.

Experimental

Analytical Procedure.—Five to 10 ml. of sample is weighed into a 100-ml. g. s. volumetric flask about one-third filled with dioxane. This mixture is made up to volume with more of the solvent, shaken until homogeneous and finally adjusted after standing at least thirty minutes in a water-bath at $25 \pm 1^\circ$. Five ml. (using calibrated pipet) of the sample solution is transferred to a 250-ml. g. s. volumetric flask and 20 ml. of the catalyst solution added.⁵

(4) Dehydration of tertiary alcohols to olefins liberates the same amount of water per hydroxyl group as esterification would do, hence it is not necessary to isolate these two effects.

(5) This solution is prepared by dissolving about 100 g. of boron trifluoride gas and 1 or 2 ml. of water in sufficient Merck C. P. glacial acetic acid to make one liter of solution. Boron trifluoride of suitable quality can be obtained in cylinders from the Ohio Chemical Company, Cleveland, Ohio.

The flask is tightly stoppered⁶ and together with a control containing 20 ml. of catalyst solution and 5 ml. of dioxane, is placed in an oven or water-bath at $67 \pm 2^\circ$ for two hours.⁷ At the end of this time the flasks are removed and allowed to cool to room temperature spontaneously. Five ml. of Baker c. P. pyridine is added to each,⁸ and the mixture titrated with Karl Fischer reagent.

After correction for water in the dioxane, catalyst and pyridine, the millimoles of water present after treatment, less the water originally present, are equal to the milliequivalents of free hydroxyl in the sample.

The water originally present may be obtained by titrating 5 ml. of the original dioxane solution with Fischer reagent. A correction must be made for the water initially present in the dioxane as this quantity is usually appreciable. The correction is made on the basis of the volume of dioxane in the aliquot figured with sufficient precision as the difference between the total volume of solution and the volume of concentrated sample employed, neglecting volume changes on mixing.

Analytical Results

The experimental results obtained with a number of alcohols and other hydroxy compounds are given in Table I. In all cases the trade products were used without further purification.

It is interesting to note that aliphatic tertiary alcohols react stoichiometrically.⁹ This reaction is undoubtedly due to both esterification and dehydration. The analysis is specific, however, since only one mole of water is released per mole of hydroxyl added.

Phenols do not esterify completely under the conditions of the general procedure. Phenol, pyrogallol and α -naphthol reacted only about 65%. An increase in catalyst concentration from 100 to 300 g. per liter raised the results with phenol to 85%. The substitution of either trimethylacetic or *n*-caproic acid for acetic acid in the catalyst solution had no appreciable effect on the phenol esterification, a recovery of about 60% being obtained in both cases.¹⁰

Terpenes react differently according to struc-

(6) A simple spring clamp (#4799), serving to prevent expulsion of the stopper on heating is furnished by the Precision Scientific Company, 1730 N. Springfield Ave., Chicago, Illinois.

(7) Methanol reacts to completion in one hour at 60° ; ethanol in two hours at 60° .

(8) The addition of pyridine just before titration with Karl Fischer reagent is essential. Its probable purpose is to destroy the activity of the catalyst and prevent esterification of the methanol of the Karl Fischer reagent. If the 5 ml. of pyridine is omitted and the activity of the catalyst is not otherwise destroyed, impossibly high titers are obtained.

(9) The tertiary hydroxyl of citric acid, however, is only 35% esterified.

(10) By using acetic anhydride in place of acetic acid, roughly quantitative results were obtained. The end-point was so obscure, because of unusual darkening of the solution, that accurate end-point adjustments were not possible. Checks of $\pm 4\%$ were an average measure of the precision to be expected.

ture. Geraniol and terpineol, the two unsaturated terpenes analyzed, gave results of 109 and 114%, respectively. Borneol, on the other hand, showed 98.4% reaction, checking the analysis by the acetyl chloride-pyridine method.²

The precision and accuracy average about $\pm 0.3\%$, comparing very favorably with the involved acetic anhydride procedures. The stoichiometric accuracy appears to be somewhat better than that of the acetyl chloride-pyridine method,² for in all cases noted, with the exception of allyl alcohol and 2-methylbutanol-4, the results were more nearly quantitative.

TABLE I
ANALYTICAL DATA FOR ALCOHOLS AND OTHER HYDROXY COMPOUNDS

Substance	% Hydroxyl compound (various methods)	Complete analysis (using Karl Fischer reagent)		
		% Hydroxyl compound	Water	% Total
Methanol	(6) ^d	99.0 \pm 0.4	0.5	99.5
Ethanol	(4)	99.5 \pm .2	.4	99.9
Ethylene glycol ^e	(2)	98.6 \pm .2	.7	99.3
<i>n</i> -Propanol ^e	(2)	98.9 \pm .4	1.2	100.1
Glycerol ^g	(2)	92.9 \pm .1	5.1	98.0
Allyl alcohol ^e	97.2 ^a (4)	96.6 \pm .3	1.9	98.5
Isobutanol	(6)	98.8 \pm .2	0.9	99.7
<i>t</i> -Butanol ^e	(6)	99.2 \pm .3	.8	100.0
2-Methylbutanol-4 ^f	97.8 ^a (6)	97.3 \pm .4	1.0	98.3
Pentanol-2 ^f	(4)	98.3 \pm .5	1.6	99.9
2-Methylbutanol-2 ^f	(4)	99.3 \pm .2	0.9	100.2
2,4-Dimethylpentanol-3	(2)	99.8 \pm .3	.2	100.0
Cyclohexanol ^e	95.0 ^a (2)	95.8 \pm .2	.0	95.8
Borneol ^e	98.4 ^a (4)	98.4 \pm .2	.0	98.4
Benzyl alcohol ^e	97.1 ^a (4)	97.3 \pm .2	1.1	98.4
Benzoin ^e	93.1 ^a (4)	97.4 \pm .2	0.0	97.4
Glycolic acid ^e	99.9 ^b (4)	100.0 \pm .3	.0	100.0
α -Hydroxyisobutyric acid ^h	97.6 ^b (2)	97.5 \pm .3	.1	97.6
Ricinoleic acid ⁱ	58.3 ^b (2)	58.9 \pm .0	1.7	60.6
Tartaric acid ^g	94.5 ^b (2)	94.1 \pm .4	0.1	94.2
Methyl glycolate	(2)	99.7 \pm .2	.1	99.8
Methyl lactate ⁱ	97.4 ^c (2)	97.5 \pm .0	.4	97.9
Ethyl lactate ^e	98.7 ^c (2)	98.5 \pm .3	.4	98.9
Ethyl tartrate ^g	94.7 ^c (2)	93.9 \pm .2	.0	93.9
Methylcellosolve ^b	93.2 ^a (2)	94.5 \pm .2	4.5	99.0

^a Acetyl chloride-pyridine procedure. ^b Alkali titration. ^c Saponification. ^d Figures in parentheses represent number of determinations. ^e Eastman Chemical. ^f Sharples Solvent Corp. ^g J. T. Baker c. P. ^h American Cyanamide Co. ⁱ Eimer & Amend Technical. ^j Eastman Practical. ^k Carbide & Carbon.

In Table II are collected results obtained with alcohols containing various quantities of water. In each case the alcohol added was calculated as the difference between the per cent. water found by analysis and 100%. It is interesting to note that reasonably accurate results were obtained with aqueous ethanol samples containing as little as 0.8% ethanol.

The procedure was exactly the same as that described above.

TABLE II
ANALYTICAL DATA FOR AQUEOUS ALCOHOL SOLUTIONS

Substance	Wt. % by difference Alcohol	Wt. % by analysis		
		Alcohol	Water	Total
Ethanol	0.8	1.0 ± 0.2	99.2 ± 0.0	100.2
Ethanol	3.9	3.9 ± .2	96.1 ± .1	100.0
Ethanol	7.6	7.4 ± .3	92.4 ± .0	99.8
Ethanol	15.8	15.6 ± .2	84.2 ± .0	99.8
Ethanol	19.4	19.0 ± .2	80.6 ± .2	99.6
Ethanol	38.9	39.0 ± .3	61.1 ± .1	100.1
Isobutanol	8.3	8.3 ± .2	91.7 ± .0	100.0
<i>t</i> -Butanol	16.2	16.0 ± .2	83.8 ± .1	99.8
<i>n</i> -Propanol	17.8	17.9 ± .2	82.2 ± .1	100.1
2-Methylbutanol-4	2.2	2.5 ± .2	97.8 ± .0	100.3
Pentanol	3.5	3.8 ± .2	96.5 ± .1	100.3

The procedure for the approximation of aliphatic alcohols in the presence of aromatic alcohols is based on the use of less concentrated catalyst solutions. Experimental results under various conditions are given in Table III.

TABLE III
ANALYTICAL RESULTS WITH ALCOHOLS USING LESS CONCENTRATED CATALYST SOLUTION

Substance	Percentage of theoretical hydroxyl			
	2 hrs. at R. T. (26 ± 1°)		2 hrs. at 60°	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
Ethanol	25	45	96.8 ± 0.3	99.0 ± 0.0
<i>n</i> -Propanol			98.7 ± .3	
Isobutanol			96.7 ± .3	
<i>t</i> -Butanol	83	93	95.5 ± .4	99.1 ± .4
Glycol			90.6 ± .2	
Glycerol			78.1 ± .2	
Cyclohexanol			55.9 ± .0	
Benzyl alcohol			97.2 ± .4	
Phenol	0.0	2.5	3.9 ± .2	26.6 ± .2
Guaiacol	0.0	2.5	4.5 ± .2	28.2 ± .5

^a Catalyst concentration 25 g./liter. ^b Catalyst concentration 50 g./liter.

The favorable results obtained with tertiary butanol at room temperature are of interest. These probably were due to dehydration since esterification to this extent seems unlikely.

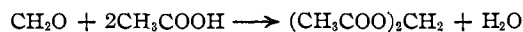
Conditions which seemed best for the analysis of aliphatic in the presence of aromatic alcohols were those of the third column of figures. Ethanol-phenol mixtures were analyzed by this procedure and the results summarized in Table IV.

TABLE IV
ANALYTICAL RESULTS ON THE DETERMINATION OF ETHANOL IN THE PRESENCE OF PHENOL

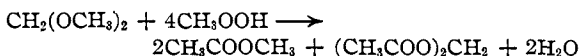
% C ₂ H ₅ OH added	% C ₂ H ₅ OH added	% C ₂ H ₅ OH found
93.3	6.7	9.0 ± 0.2
57.0	43.0	43.8 ± .2
11.1	88.9	88.2 ± .1

It is believed that the results obtained with phenol and guaiacol are typical of what may be expected with other phenols and that the degree of differentiation would be much like that in Table IV. As previously noted, using the general catalyst solution, pyrogallol and α -naphthol react to about the same extent as phenol.

Interfering Substances.—The new hydroxyl procedure is unfavorably affected by the presence of a few classes of organic compounds. Aldehydes and ketones react to a considerable extent, *e. g.*, formaldehyde (37% aqueous) and cyclohexanone showed about 70 and 50% reaction, respectively. The reaction with carbonyl compounds in general is probably analogous with that proposed for formaldehyde



Acetals and ketals react nearly to completion assuming two moles of water are formed for each mole of sample. For methylal the reaction can be written as



Analyses of methylal, acetal and di-*n*-butyl formal on this basis gave results of 92, 91 and 88%, respectively.

Most amines interfere with the method, by affecting catalyst activity.

Summary

1. A specific quantitative method for the determination of hydroxy compounds has been described. The method is based on quantitative esterification and subsequent titration of the water liberated, using the highly specific Karl Fischer reagent.

2. Analytical results for more than twenty-five hydroxy compounds, principally aliphatic, are tabulated.

3. The method is quantitative for samples containing large excesses of water.

4. Tertiary aliphatic alcohols may be analyzed by this procedure.

5. A quantitative method for the determination of aliphatic alcohols in the presence of phenols is described.