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Analytical Procedures Employing Karl Fischer Reagent.¹ IV. The Determination of Acid Anhydrides

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Many of the older methods of determining anhydrides of carboxylic acids do not distinguish sharply between anhydride and free acid. A procedure developed by the senior authors² avoids this difficulty by a scheme based on separate titrations with sodium hydroxide and sodium methylate. This method, however, is subject to interference by easily hydrolyzed esters and certain acidic inorganic compounds.

Recent studies of the versatile Karl Fischer reagent have led to the development of new quantitative procedures for hydroxyl³ and carboxyl⁴ compounds, and now a similar method for anhydrides has been completed. This application depends on the hydrolysis of the anhydride in acetic acid solution under the influence of boron trifluoride. Introduction of a known quantity of water, somewhat in excess of stoichiometric requirements, and determination of the residual water by titration with Karl Fischer reagent permit an exact correlation of anhydride content with water removal according to the equation, $\text{RCO-OCOR} + \text{H}_2\text{O} = 2\text{RCOOH}$.

Unlike the acidimetric procedures free acids do not react and easily hydrolyzed esters remain un-

changed due to the relatively low water concentration and the great excess of acid present. Substances interfering with the hydroxyl procedure⁸ also affect the new anhydride method.

A group of thirteen anhydrides were analyzed by this method and checked by the sodium hydroxide-sodium methylate procedure.² The precision and accuracy are usually within $\pm 0.3\%$. Experimental results are given in Table I.

Although glutaric anhydride hydrolyzed quantitatively, other anhydrides derived from dibasic acids failed to react completely. Results with maleic, phthalic and succinic anhydrides showed 0, 11 and 91% hydrolysis, respectively.

Changes in catalyst concentration had a marked effect on these anhydrides, as indicated by data given in Table II.

TABLE II

HYDROLYSIS OF ANHYDRIDES USING CATALYST SOLUTIONS OF VARIOUS CONCENTRATIONS^a

Anhydride	% Hydrolysis ^b					
	100 g.	50 g.	25 g.	15 g.	5 g.	0 g.
Acetic	100.0		98.0			
Caproic	100.0		97.0			
Succinic	91.2	95.4	99.5	93.2	63.9	27.1
Maleic	0.0	1.0	2.3	42.0	36.5	24.5
Glutaric	100.0	100.0	100.0	100.0	93.7	47.6
Phthalic	10.9	13.8	15.5	18.7	16.9	14.0

^a Catalyst concentration expressed as grams per liter of solution. ^b All results corrected for inert diluents.

From an examination of Table II it is evident that in isolated cases a procedure could be devised for distinguishing between certain anhydrides. For such cases control experiments should be run as a means of fixing the relative error.

Although the anhydrides in dioxane solution react only partially with the carboxyl catalyst,⁴ the aliphatic acid anhydrides in methanol solution react quantitatively. The probable reactions



liberate one mole of water per mole of anhydride. Representative results, after correction for free acidity, are given in Table III.

It is interesting to note that maleic and succinic anhydrides react stoichiometrically under these conditions, whereas hydrolysis, as stated

TABLE I

ANALYTICAL DATA FOR ANHYDRIDES

Anhydride	% of theoretical catalytic hydrolysis	--CO--O--CO-- NaOH- NaOCH ₃
Acetic (6) ^a	100.0 \pm 0.2	99.9
Propionic (4)	97.0 \pm 0.3	97.2
<i>n</i> -Butyric (2)	85.5 \pm 0.5	85.4
Crotonic (2)	89.6 \pm 0.0	
<i>n</i> -Valeric ^b (2)	2.0 \pm 0.4	1.9
Caproic (2)	78.6 \pm 0.4	78.4
Heptylic (2)	92.0 \pm 0.3	92.1
Glutaric (2)	95.3 \pm 0.3	95.5
Benzoic (4)	99.0 \pm 0.3	99.2
Furoic (4)	95.1 \pm 0.5	94.8

^a Figures in parentheses indicate number of individual determinations. ^b Old sample, mainly *n*-valeric acid, used to test method in low anhydride range.

(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, *ibid.*, **58**, 2452 (1936).

(3) Bryant, Mitchell and Smith, *ibid.*, **62**, 1 (1940).

(4) Mitchell, Smith and Bryant, *ibid.*, **60**, 4 (1940).

TABLE III
ANALYTICAL DATA FOR ANHYDRIDES

Anhydride	% of Theoretical Carboxyl catalyst ⁴	--CO--O--CO-- NaOH-NaOCH ₃
Acetic	100.3 \pm 0.3	99.9
Propionic	97.1 \pm 0.3	97.2
Succinic	94.2 \pm 0.4	94.5
Maleic	90.0 \pm 0.2	90.0

above, is incomplete. As would be expected, the aromatic anhydrides only partially react.⁴

In the course of the present research several nitrogen bases, including pyridine and tri-*n*-butylamine, were substituted for the acid catalyst solution. It was previously thought that hydrolysis of acid anhydrides in the presence of slightly more than the theoretical quantity of water would be complete where large excesses of these bases are used. However, the anhydrides studied, with one exception, failed to react completely on heating at 100° for periods up to four hours. The exception was acetic anhydride, which hydrolyzed quantitatively in one hour at 60° using pyridine as the base.

Some experiments on the dehydration of glacial acetic acid by means of the anhydride without any catalyst or acid acceptor are of interest. The acid containing about half a per cent. of water was mixed with slightly more than the calculated amount of acetic anhydride required to produce anhydrous acid. The mixture was allowed to stand at room temperature and was analyzed at intervals by the Karl Fischer procedure. The following results were obtained.

Wt. % H ₂ O	Time, standing at room temperature
0.54	0
.52	4 min.
.47	1.5 hrs.
.36	4.5
.08	21
.015	48

The reaction is slow but proceeds to completion without a catalyst.

Experimental

Compounds Investigated.—With two exceptions all of the anhydrides studied in the present investigation were Eastman Kodak Co. products, and were used without further purification. The *n*-valeric anhydride was an old sample which was used primarily to determine the precision of the method for small quantities of anhydride.

Phthalic anhydride ("Aero" Brand) was obtained from American Cyanamide Corp., and glutaric anhydride was prepared from the acid by the method of Mol.⁵ In order to prevent adsorption of water vapor, a simple "dry manipulator" was used to dispense the solid anhydrides.²

Analytical Procedure.—Five to 10 ml. of sample is weighed into a 100-ml. g. s. volumetric flask about one-third filled with Merck c. p. glacial acetic acid. The solution is adjusted to volume with more acetic acid, after thermostating at 25 \pm 1°. Five ml. (using calibrated pipet) of this solution is transferred to a 250 ml. g. s. volumetric flask and 20 ml. of catalyst solution added.⁶ The flask together with a blank containing 5 ml. of acetic acid and 20 ml. of catalyst solution is placed in a water-bath at 60 \pm 1°. The stopper is loosened momentarily to allow for expansion of included air, tightened and heated for two hours. After the flasks have been allowed to cool spontaneously to room temperature and 5 ml. of Baker c. p. pyridine is added, the excess water is titrated with Karl Fischer reagent. The total anhydride is measured by the difference between the water added, *i. e.*, the water content of the blank, and the water found by titration after reaction.

Summary

1. A quantitative procedure for the determination of carboxylic acid anhydrides has been described. The method depends on complete hydrolysis of the anhydride in the presence of excess water and subsequent titration of the residual water with Karl Fischer reagent. It is best suited for the determination of acyclic aliphatic anhydrides.

2. Analytical data for ten anhydrides are tabulated.

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(5) Mol, *Rec. trav. chim.*, **26**, 373 (1907).

(6) The catalyst solution is prepared by dissolving 100 g. of boron trifluoride gas and 4 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.