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Analytical Procedures Employing Karl Fischer Reagent.[1] VII. Alternative Method for the Determination of Acid Anhydrides

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A quantitative procedure for the determination of anhydrides by acid hydrolysis using Karl Fischer reagent has been described in a previous publication.[2] A second and more widely applicable method based on the use of this reagent has now been developed, and like the earlier procedure is in most cases unaffected by the presence of acidic inorganic compounds.[3] Similarly, there is no interference from easily hydrolyzed esters due to the relatively low water concentration of the reagent.

The new method depends on hydrolysis of the anhydride in the presence of pyridine, using sodium iodide as catalyst, according to the equation

$$RCOOCOR + H_2O = 2RCOOH$$

Eleven anhydrides were analyzed by the new method and the results checked by either the sodium hydroxide–sodium methylate[4] or acid hydrolysis procedure.[2] The precision and accuracy are usually within ±0.3%. Experimental results are given in Table I.

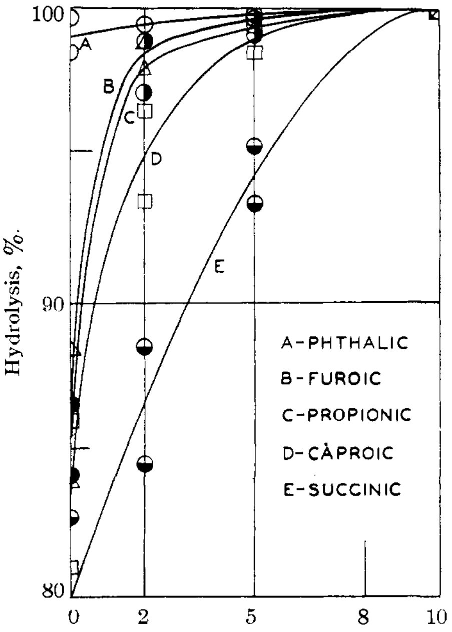

Fig. 1.—Effect of concentration of sodium iodide on hydrolysis of anhydrides.

TABLE I

ANALYTICAL DATA FOR ANHYDRIDES

Anhydride	% Anhydride NaI catalyzed hydrolysis	Acid hydrolysis	NaOH–NaOCH$_3$
Acetic	(8)[a] 99.5±0.4		99.5
Propionic	(4) 97.4±0.2	97.2	
n-Butyric	(2) 98.3±0.3		98.3
Crotonic	(2) 87.3±0.1	87.1	
Caproic	(4) 95.0±0.2		94.8
Heptylic	(4) 89.1±0.3	89.2	
Succinic	(4) 91.0±0.5		90.9
Glutaric	(2) 100.1±0.2	100.0	
Benzoic	(5) 89.7±1.0		89.8±0.5
Phthalic	(2) 98.9±0.2		98.4
Furoic	(2) 94.9±0.2	94.9	

[a] Figures in parentheses represent number of individual determinations.

Most anhydrides derived from dibasic acids reacted quantitatively, whereas by the acid hydrolysis procedure[2] only the glutaric derivative gave stoichiometric results in the group of four examined. However, maleic anhydride reacted violently with the pyridine reagent, probably combining with the pyridine by a Diels–Alder mechanism. Camphoric was the only other anhydride tried which failed to react quantitatively. Due to steric hindrance hydrolysis was only about 1% complete. The crystals of benzoic anhydride used were coated with benzoic acid. This no doubt explains the relatively poor precision obtained in the five determinations recorded.

During the previous research[2] several nitrogen bases were substituted for the acid catalyst solution, but without the addition of sodium iodide. Under these conditions the anhydrides studied failed to react completely. In several experiments using pyridine as the base acetic anhydride was observed to hydrolyze quantitatively in one hour at 60°. Later results, however, were variable (98–100%) and it is concluded that this procedure is not dependable in the absence of the sodium iodide catalyst.

By employing a catalyst in the presence of excess pyridine, hydrolysis was made quantitative. Sodium iodide proved to be best suited in this

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[1] See the first paper of this series, Smith, Bryant and Mitchell, THIS JOURNAL, **61**, 2407 (1939).

[2] Smith, Bryant and Mitchell, *ibid.*, **62**, 608 (1940).

[3] Mitchell, Smith and Bryant, *ibid.*, **62**, 4 (1940).

[4] Smith and Bryant, *ibid.*, **58**, 2452 (1936).

capacity since it is soluble in pyridine and also inert toward Karl Fischer reagent. The type of catalysis involved is not known, but the high electrical conductivity of sodium iodide in pyridine solution observed in this Laboratory may have some bearing upon its catalytic activity. In Fig. 1 the effect of increasing concentrations of sodium iodide on hydrolysis is shown; curves for five representative anhydrides are presented. It is interesting to note that hydrolysis of phthalic anhydride was 99% complete even without sodium iodide.

Compounds Investigated.—All anhydrides were used without further purification. Glutaric anhydride was prepared from the acid by the method of Mol.[5] Phthalic anhydride (Aero Brand) was obtained in flake form from American Cyanamid Corporation. All others were Eastman Kodak Co. chemicals. As in the previous investigations, a simple "dry manipulator" was used to dispense the solid anhydrides.[2]

Reagents.—Ten per cent. sodium iodide in pyridine containing about 1% of water was prepared by making 100 g. of Baker C. P. analyzed sodium iodide and 8 ml. of water up to 1 liter with Baker C. P. pyridine.

Analytical Procedure.—A sample containing 8–10 millimoles of anhydride is weighed into a 250-ml. glass-stoppered volumetric flask. Using a precision pipet, 25 ml. of the pyridine reagent is added. The flask, together with a blank containing 25 ml. of the reagent, is placed in a water-bath at 60 ± 1°. The stoppers are loosened momentarily to allow for expansion of included air, tightened, and the flasks heated for one hour. After being allowed to cool spontaneously to room temperature, the excess water is titrated with Karl Fischer reagent. The total anhydride is measured by the difference in titer between water added (blank titer) and water found by titration after reaction.

Interfering Substances.—Easily hydrolyzed esters, as stated above, do not interfere. This was established in experiments with methyl formate, methyl acetate and ethyl acetate.[6] Since at low temperatures (0° or below) the reaction of anhydrides with water is generally very slow, the water content can be obtained by direct titration of the chilled sample with Fischer reagent. When this water is taken into consideration, analyses by the above method will give the correct anhydride content of such mixtures.

Summary

1. An alternative procedure for the quantitative determination of carboxylic acid anhydrides has been described. The method depends on complete hydrolysis of the anhydride by a small excess of water in the presence of pyridine, with sodium iodide as a catalyst, and subsequent titration of the residual water with Karl Fischer reagent.

2. Analytical data for eleven anhydrides are tabulated.

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

[6] The determination of anhydride in the presence of carbonyl compounds is being investigated.

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Thermal Reactions Promoted by Diacetyl[1]

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In a number of investigations it has been shown that free radicals produced either thermally,[3] or photochemically,[4] can markedly accelerate the decomposition of other compounds and frequently can induce decomposition at temperatures at which the pure compound alone is stable. However, the introduction of methyl groups into acetone at 400° or below does not initiate a chain decomposition of acetone.[4,5] On the other hand, in the present study of the effect of diacetyl on the decomposition of acetone at 526°, it was discovered that a small amount of diacetyl accelerates the decomposition. Presumably this indicates that diacetyl acts as a source of free radicals in the neighborhood of 500° just as azomethane[3b] and ethylene oxide[3c] do at lower temperatures. Therefore, an investigation of the influence of small quantities of diacetyl on the rate of decomposition of various organic compounds, as well as on the polymerization of ethylene, was undertaken.

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[1] In part from a dissertation submitted by W. D. Walters to the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] (a) Frey, *Ind. Eng. Chem.*, **26**, 200 (1934); (b) Allen and Sickman, THIS JOURNAL, **56**, 2031 (1934); (c) Fletcher and Rollefson, *ibid.*, **58**, 2135 (1936); (d) Echols and Pease, *ibid.*, **58**, 1317 (1936).

[4] Leermakers, *ibid.*, **56**, 1899 (1934).

[5] Rice, Rodowskas and Lewis, *ibid.*, **56**, 2497 (1934).