[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A GASOMETRIC METHOD FOR THE DETERMINATION OF ACETIC ANHYDRIDE[1]

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Introduction

The extensive use of acetic anhydride in the cellulose ester industry and in other fields as an acetylating agent makes a method for the rapid estimation of the anhydride highly desirable. The methods which are now largely in use involve rather laborious titrations and in many cases necessitate hours for their performance. Notable among these are (1) the method of Reclaire,[2] (2) the method of Menschutkin and Vasilieff,[3] and (3) the method of Edwards and Overton.[4] Walton and Withrow[5] devised a method for the estimation of acetic acid in the anhydride based upon the inhibiting action of the acid on the catalytic decomposition of formic acid. This method, while extremely rapid is applicable only to samples containing 5% or less of acetic acid.

In a recent communication[6] it was noted that oxalic acid is rapidly decomposed in pyridine solutions by acetic anhydride with the concomitant evolution of carbon dioxide and carbon monoxide. It was further noted that *the amount of oxalic acid decomposed is directly proportional to the amount of acetic anhydride added.* These facts suggested the possibility of a gasometric method for the determination of the anhydride.

Experimental Part

The apparatus used was essentially that described in the study of the decomposition of oxalic acid by acetic anhydride. The gases were collected in calibrated 100cc. burets over water saturated with carbon monoxide and carbon dioxide. No precautions were taken in purifying pyridine from its derivatives but great care was taken in drying it. Fused sodium hydroxide and barium oxide were employed as described in the previous paper. The pyridine was then further treated with calcium carbide and distilled directly into the reaction flasks. The distillate showed that small amounts of acetylene were present when tested by the method of

[1] The work included in this paper is from the thesis presented by Earl L. Whitford in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. This investigation was conducted under the supervision of Professor J. H. Walton.

[2] Reclaire, *Perfumery Essent. Oil Record*, 13, 148 (1922).

[3] Menschutkin and Vasilieff, *J. Russ. Chem. Soc.*, 21, 195 (1895).

[4] Edwards and Overton, *J. Chem. Soc.*, 99, 1181 (1911).

[5] Walton and Withrow, THIS JOURNAL, 45, 2689 (1923).

[6] Whitford, THIS JOURNAL, 47, 2934 (1925).

Weaver.[7] After the pyridine had been saturated with dry carbon monoxide and dioxide, an excess of anhydrous oxalic acid was added and the mixture subjected to a preliminary shaking. In the meantime, samples of acetic anhydride were weighed into glass capsules carefully protected from the air and these were then dropped into the reaction mixture. Immediately, carbon monoxide and carbon dioxide were evolved at a very rapid rate, the reaction being practically complete in 15 minutes. Blanks containing pyridine, treated in the same manner as in the quantitative determination, with oxalic acid in one flask and acetic anhydride in the other, showed no evolution of gas. When the acetic anhydride was all used and no more gas was evolved, the total volume was noted, and calculated in terms of acetic anhydride on the basis of the following reaction: $(COOH)_2 + (CH_3CO)_2O \longrightarrow CO + CO_2 + 2CH_3COOH$. Tables I and II show the results of the analysis of pure acetic anhydride prepared by the method of Walton and Withrow and of Baker's 92% commercial product.

TABLE I

ANALYSIS OF PURE ACETIC ANHYDRIDE (WALTON AND WITHROW)

Temperature, 28° Pressure, 743 mm.

Sample G.	Gas Cc.	Calcd. ac. anhyd.	% ac. anhyd.
0.1942	100.0	0.1944	100.1
.1711	88.0	.1710	99.9
.1694	87.2	.1695	100.0

TABLE II

ANALYSIS OF ACETIC ANHYDRIDE (BAKER'S 92%)

Temperature, 28° Pressure, 743 mm.

Sample G.	Gas Cc.	Calcd. ac. anhyd.	% ac. anhyd.
0.1985	93.75	0.1823	91.9
.1898	89.8	.1749	92.1

Walton and Withrow found that acetic anhydride prepared by their method was approximately 99.97% pure. The method here devised has the advantage of being extremely rapid and at the same time is accurate to within 0.1–0.2%. The experimental error could very likely be reduced even more if a buret of a greater capacity than 100 cc. were employed, thus permitting the analysis of larger samples of acetic anhydride. The pyridine may be recovered for further use by simply dehydrating it again, so that no expensive reagents need be lost.

Summary

1. A gasometric method for the determination of acetic anhydride has been devised based upon the decomposition of oxalic acid in pyridine solutions. The method is both rapid and accurate.

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[7] Weaver, THIS JOURNAL, **36**, 2462 (1914).