acid which crystallized in plates that melted at 157–159°. The anilide prepared from this acid, after crystallization from alcohol and from water, melted at 122–123°.

The α-phenoxyhydracrylic acid obtained was purified by crystallization from toluene and from water, the usual crystallization from chloroform being omitted because of the small quantity in hand; the product formed needles melting at 102–106°; yield, 0.083 g. A mixture with an equal amount of the pure acid (m. p. 109–110°) melted at 103–106°.

The assistance of Professor S. M. McElvain is gratefully acknowledged.

Summary

The reaction between sodium phenoxide and α-chlorohydracrylic acid is shown to yield a mixture of α-phenoxyhydracrylic acid and β-phenoxylactic acid in which the latter predominates greatly.

This is in agreement with the prediction based on the behavior of α-chlorohydracrylic acid toward ammonia and indicates that the α-phenoxyhydracrylic acid formed in the reaction between sodium phenoxide and β-chlorolactic acid does not owe its origin to the presence of α-chlorohydracrylic acid as an impurity in the β-chlorolactic acid.

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[Contribution from the Laboratory of General Chemistry of the University of Wisconsin]

THE DETERMINATION OF THE PURITY OF ACETIC ANHYDRIDE

By Chester K. Rosenbaum and James H. Walton

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Introduction

A rapid and accurate method for the quantitative determination of acetic anhydride is of great practical importance because of the extensive industrial uses of this reagent. In a publication by Whitford[1] and the senior author of this paper it was shown that anhydrous oxalic acid is decomposed quantitatively in the presence of pyridine, acting as a catalyst, according to the equation

$$(COOH)_2 + (CH_3CO)_2O = CO_2 + CO + 2CH_3COOH$$

This reaction had been reported by Dr. Schierz[2] of this Laboratory, who observed that various tertiary bases such as picolines, butidine, collidine, etc., could also be used as catalysts. Whitford found that the pyridine acts as a catalyst for the reaction through the formation of pyridine acid oxalate $C_5H_5N\cdot(COOH)_2$ which is subsequently decomposed by the acetic anhydride.

The carbon dioxide and carbon monoxide evolved in the reaction were measured by Whitford to give a gasometric method for the determination of acetic anhydride. He found his method to be accurate to within 0.1%

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[1] Whitford and Walton, This Journal, **47**, 2934, 2939 (1925).

[2] Schierz, *ibid.*, **45**, 455 (1923).

for samples of pure acetic anhydride and also for 92% acetic anhydride. In the present investigation the same reaction was used but instead of measuring the gases evolved, the excess oxalic acid was determined by a potassium permanganate titration.

Procedure

About one gram of different samples of acetic anhydride was weighed from a weighing pipet into a wide-mouthed glass-stoppered bottle containing about one gram of anhydrous oxalic acid prepared by the method of Hultman, Davis and Clark.[3] Two cc. of pyridine dried over barium oxide and calcium hydride was then added and the bottle kept cool in water for five minutes to prevent vaporization of the acetic anhydride. After standing for ten minutes longer at about 50°, the excess oxalic acid was titrated with *N*/10 potassium permanganate. The results were checked by the standard alkalimetric titration carried out as follows.

About 170 cc. of 0.1351 *N* sodium hydroxide was measured from a buret into a flask and about one gram of acetic anhydride was then weighed into the sodium hydroxide solution from a weighing pipet. The anhydride was allowed to hydrolyze at 40° for eight hours and the excess sodium hydroxide then titrated with *N*/10 hydrochloric acid. The results were calculated by the method described by Scott.[4]

RESULTS

Sample	Percentage of acetic anhydride	
	$(COOH)_2$ method	NaOH titration
A	79.01	79.15
B	86.52	86.2
C	92.19	91.7

Notes.—All materials were tested for oxidizing and reducing substances and if any were present, a blank was run. Other acids or acid-forming materials in the acetic anhydride did not affect the oxalic acid method but did give high results when an alkalimetric titration was run with certain samples of commercial anhydride. In an alkalimetric titration of a one-gram sample, the presence of 0.2% of acetyl chloride will raise the calculated percentage of acetic anhydride by 1%. The presence of small amounts of acetyl chloride, however, does not affect the oxalic acid method. Similarly an error of only 0.1 cc. of *N*/10 sodium hydroxide will change the calculated percentage of acetic anhydride by about 0.4%. The other standard methods[5] are more accurate than an alkalimetric titration but require considerable time and care.

The purity of the anhydrous oxalic acid used in this investigation was found to be 99.84% by a potassium permanganate titration. The presence of a small percentage of water in the oxalic acid apparently does not vitiate the results, as is evidenced by the fact that 99.69% pure anhydrous oxalic acid when used gave correct values. This is explained by the fact

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[3] Hultman, Davis and Clark, THIS JOURNAL, **43**, 366 (1921).

[4] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, New York, **1922**, Vol. II, p. 1054.

[5] See Radcliffe and Medofski, *J. Soc. Chem. Ind.*, **36**, 628 (1917).

that the reaction between oxalic acid and acetic anhydride is so rapid that the water does not have opportunity to react with the anhydride. The only considerable error that can be introduced was found to be a lowering of the results caused by the vaporization of the anhydride due to the heating when pyridine was added. This error varied from 0.2 to 0.5% but is avoided by cooling the container. The amount of pyridine added was varied from 1 to 5 cc. with no effect on the results. An error of 0.1 cc. in the potassium permanganate titration causes a deviation of only 0.05%.

Summary

A method has been devised for the determination of the purity of acetic anhydride based on the decomposition of anhydrous oxalic acid by acetic anhydride using pyridine as a catalyst, and subsequently determining the excess oxalic acid with potassium permanganate. The method is simple, rapid and easily accurate to within 0.1%.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SYMMETRICAL DIALKYL-TETRA-TERTIARY-BUTYLETHINYLETHANES

BY H. B. GILLESPIE AND C. S. MARVEL

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Recent work by Ziegler and Schnell[1] and by Conant and his students[2] has indicated that certain dialkyl-tetra-arylethanes have properties that resemble quite closely those of the hexa-arylethanes. In particular, it has been found that a tertiary butyl group or a cyclohexyl group can replace a phenyl group without greatly changing the amount of dissociation of the ethane. Work in this Laboratory on the acetylenic ethanes has shown that hexa-*tert.*-butylethinylethane[3] (I) is cleaved by 1% sodium amalgam and resembles in this respect the hexa-arylethanes. Rossander and Marvel[4] have observed that diphenyl-tetra-*tert.*-butylethinylethane (II) requires 40% sodium amalgam for cleavage and hence is more stable toward alkali metals than is the hexa-acetylenic compound. The series of tetra-acetylenic ethanes has now been extended to include di-*tert.*-butyl-tetra-*tert.*-butylethinylethane (III) and dicyclohexyl-tetra-*tert.*-butylethinylethane (IV).

$$[(CH_3)_3C{-}C{\equiv}C]_3{-}C{-}C[C{\equiv}C{-}C(CH_3)_3]_3$$

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[1] Ziegler and Schnell, *Ann.*, **437**, 252 (1924).

[2] Conant and Small, THIS JOURNAL, **47**, 3068 (1925); Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926); Conant and Bigelow, *ibid.*, **50**, 2041 (1928).

[3] Salzberg with Marvel, *ibid.*, **50**, 1737 (1928).

[4] Rossander and Marvel, *ibid.*, **51**, 932 (1929).