

Gerald A. Clark M.S. 1951

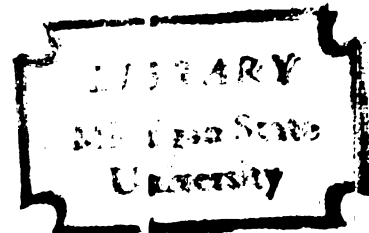


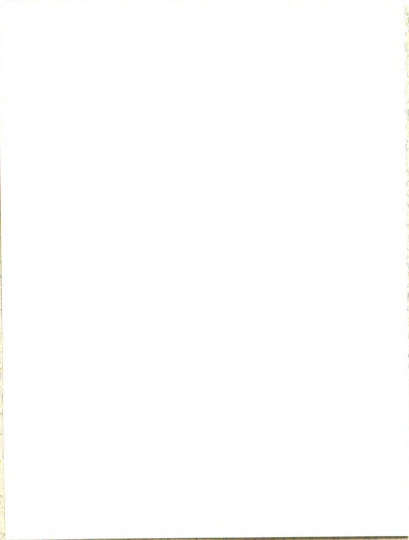
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THE FORMATION OF ALKYLIDENE  
DIACETATES FOR THE QUANTITATIVE  
ESTIMATION OF ALDEHYDES

Thesis for the Degree of M. S.  
MICHIGAN STATE COLLEGE  
Gerald A. Clark  
1951

THESIS







THE FORMATION OF ALKYLIDENE DIACETATES  
FOR THE QUANTITATIVE ESTIMATION  
OF ALDEHYDES

By

Gerald A. Clark

A THESIS

Submitted to the School of Graduate Studies of  
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1951

THE FORMATION OF ACYLIDES DEVELOPED  
FOR THE QUANTITATIVE DETERMINATION  
OF ALDEHYDES

By

Gerald A. Clark

An abstract of the thesis for the degree  
MASTER OF SCIENCE

In this work an attempt is made to develop a method for the quantitative determination of aldehydes based on a boron trifluoride catalyzed reaction between aldehydes and aliphatic acid anhydrides (1).

An excess of acetic anhydride is allowed to react with the aldehyde in the presence of a small amount of boron trifluoride etherate using benzene as the solvent. After the reaction is completed the excess acetic anhydride is titrated with standard sodium methyrate. Thymol blue indicator was found to give a favorable color change at the endpoint. The addition of dimethyl aniline before titration appeared to improve the endpoint by co-ordinating the excess boron trifluoride. Benzaldehyde was found to react much slower than the lower aliphatic aldehydes in a benzene solvent.

(1) E. H. Ren, J. J. Sanderson and C. R. Hauser, J. Am. Chem. Soc. 72, 247 (1949).

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# ACKNOWLEDGMENT

This author wishes to express his appreciation to Dr. Kenneth G. Stone for his encouragement and assistance during this work.

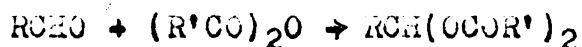
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## CONTENTS

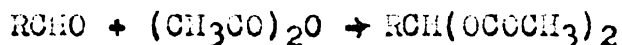
	PAGE
INTRODUCTION.....	1
EXPERIMENTAL AND RESULTS.....	3
Pyridine as the solvent.....	3
Dioxane as the solvent.....	5
Benzene as the solvent.....	7
Endpoint detection.....	8
Determination of reaction conditions.....	10
Determination of aldehydes.....	14
DISCUSSION.....	18
SUMMARY.....	23
REFERENCES.....	24

## INTRODUCTION

The formation of alkylidene diacetates (di-esters of the type  $\text{RCH}(\text{OCOR}')_2$ ), has been known since 1857 (1). They have been prepared by heating alkylidene dihalides with salts of appropriate acids, (2) or by heating aldehydes with suitable acid anhydrides in the presence of small amounts of sulfuric acid. (3)



In a recent publication by Man, Sanderson and Hauser, (4) it was shown that alkylidene diacetates could be prepared in good yield by a boron trifluoride catalyzed addition of aliphatic acid anhydrides to aldehydes. The overall reaction was shown to be:



Less than 20 drops of boron trifluoride etherate containing 45 % boron trifluoride to 0.5 moles of the aldehyde were required to give products in yields of the order of 80 % after extraction and fractionation. Hauser and his co-workers investigated both aromatic and aliphatic aldehydes including acetaldehyde, propionaldehyde, isobutyraldehyde and benzaldehyde. They successfully used acetic, propionic, and butyric anhydrides. The reaction appeared to fail with succinic anhydride and propionaldehyde. Also Hauser and Adams (6) had previously found that the reaction between acetic anhydride and ketones to form  $\beta$ -diketones required an equimolar amount

of boron trifluoride.

The reaction using aldehydes appeared to fulfill requirements which have recently been set forth by Siggia as essential for a reaction to be useful as a basis of a method for the quantitative determination of a functional group (5). Acetic anhydride which is easily measured by common analytical means is consumed and the reaction appears to approach completion.

It was necessary to find a suitable solvent and indicator, and to determine the optimum conditions for quantitative results since the analytical approach had not been investigated previously. Also it appeared advisable to investigate the possibility that ketones would not significantly interfere in the reaction between acetic anhydride and aldehydes in which only a very small amount of the boron trifluoride was used.

## EXPERIMENTAL AND RESULTS

The reaction between an aldehyde and acetic anhydride in the presence of boron trifluoride can be considered as an esterification of the ortho form of the aldehyde (7). With this assumption in mind, an attempt was made to set up a procedure for the determination of aldehydes adapted from the acetic anhydride method of Ogg, Porter and Willits for the quantitative esterification of alcohols (8).

## 1. Pyridine as the Solvent

In the presence of a basic solvent such as pyridine, weak acids act as stronger acids and are more easily determined by acid-base titrations.

Reagents:

Boron trifluoride etherate was prepared at first by the method used by Laubengayer and Finlay (9). Ether which was dried over sodium, was heated in a one liter round bottom flask fitted with 7 mm. glass tubing which led to a 3 necked, one liter reaction flask which was equipped with a glass escape jet and a glass tube leading to a cylinder of boron trifluoride. The reaction vessel was chilled in ice water throughout the reaction. It was swept with ether vapor for 8 - 10 minutes, after which boron trifluoride was passed in, mixing with the continuous flow of ether vapor at such a rate that white fumes were noticed at the escape jet. The reaction was continued for  $\frac{1}{2}$  hour, after which the introduction of boron trifluoride was discontinued while the flow of ether was continued for 5 - 8 minutes. In later work a commercial



preparation of boron trifluoride etherate containing 48 % boron trifluoride of technical grade was used.

A standard alcoholic sodium hydroxide solution was prepared by diluting 60 ml. of a saturated solution of sodium hydroxide to two liters in methyl alcohol and standardizing against potassium acid phthalate to a phenolphthalein endpoint.

Pyridine and acetic anhydride were freshly distilled and mixed in a ratio of 3 volumes of pyridine to 2 volumes of acetic anhydride.

Procedure:

Samples of propionaldehyde were weighed in small glass ampoules which were placed in 150 ml. glass stoppered Erlenmeyer flasks. Three ml. of the acetic anhydride - pyridine reagent and 0.2 ml. of boron trifluoride etherate were added by pipet.

The flasks were chilled in ice water for 10 minutes to prevent loss of the volatile aldehyde after which the glass ampoules were broken and the flasks immediately stoppered and placed on an automatic shaker. After two hours the flasks were removed, 5 ml. of water were added and the flasks were shaken for an additional 10 minutes. The sides of the flasks were then rinsed down with 3 ml. of pyridine and titrated with standard alcoholic sodium hydroxide. The color change of a mixed indicator of cresol red and thymol blue was taken as the endpoint (8).

This method and variations of it gave low and inconsistent results. Typical results obtained using pyridine as a solvent are shown in Table I:

Table I

ml. of 3.1 solution of pyridine - acetic an- hydride	wt. of propional- dehyde sample	ml. boron trifluoride etherate added	reaction time	% propionalde- hyde calculated
4.0	0.0505 gm.	0.2 ml.	1 hr.	50.9 %
4.0	0.0932 gm.	0.2 ml.	1 hr.	48.1 %
5.0	0.4570 gm.	0.2 ml.	1 hr.	15. %
5.0	0.5793 gm.	0.2 ml.	1 hr.	11. %

It was assumed that pyridine interfered in the reaction by causing aldol type condensation or by co-ordinating the boron trifluoride. Pyridine was therefore abandoned as a solvent.

## 2. Dioxane as the Solvent

It was felt that dioxane, while providing a solvent for the acetic anhydride and aldehyde, would permit hydrolysis of the excess acetic anhydride after the reaction was complete. A series of experiments using 1,4-dioxane as a solvent were next carried out. The dioxane was refluxed over sodium and redistilled. A variety of concentrations of acetic anhydride and boron trifluoride were tried using the same general procedure as for pyridine. Results were again low and erratic.

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Because boron trifluoride is hydrolyzed so readily by water, a series of experiments were tried in which water was not added to hydrolyze the excess acetic anhydride. The excess acetic anhydride was titrated with a standard solution of sodium methylate in absolute methyl alcohol. One mole of acetic anhydride consumes one mole of sodium methylate whereas a mole of acetic anhydride requires 2 moles of sodium hydroxide.

In the absence of pyridine an indicator was required which changed color at a higher pH range. Phenolphthalein was used but the color change to red was difficult to see due to the amber color of the reaction mixture. Thymol blue was then used and the color change at the endpoint was discernible. The results obtained by the methods using dioxane were again low and inconsistent. Typical results using dioxane as a solvent are shown in Table II. A reagent was prepared by pipetting 20 ml. of acetic anhydride and 3 ml. of boron trifluoride into 30 ml. of dioxane. Five ml. aliquots were pipetted into 250 ml. Erlenmeyer flasks containing weighed samples of propionaldehyde in glass ampoules. Blanks were prepared in the same manner. After reaction the sides of the flasks were rinsed with 5 ml. of dioxane, 4 drops of a 1 % solution of thymol blue in methanol were added, and the mixture titrated with 0.4100 N. sodium methylate solution.

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Table II

Sample weight	Reaction time	% Protonaldehyde calculated
0.0443 gm.	4 hrs.	80.5
0.0425 gm.	4 hrs.	33.5
0.0575 gm.	4 hrs.	54.1
0.0575 gm.	4 hrs.	78.5

The endpoint faded rapidly even when titrations were carried out under a nitrogen atmosphere. This indicated that interference was not caused by atmospheric moisture. Higher results were obtained with larger excesses of acetic anhydride, but were even more inconsistent.

Since boron trifluoride forms molecular compounds, or complexes with many organic oxygen or nitrogen containing compounds (10), it appeared that the pyridine and dioxane solvents were interfering by co-ordinating the boron trifluoride catalyst. Thus a solvent which did not have oxygen or nitrogen to co-ordinate the boron trifluoride would be advantageous in order to satisfy all requirements. The solvent must also be inert toward acetic anhydride and sodium methylate.

### 3. Benzene as the Solvent

Benzene is not affected by boron trifluoride although Friedel-Craft type reactions may be carried out using boron trifluoride as the catalyst. It was assumed that under the

conditions used that this interference would be negligible. If a blank is carried along with the sample, any slight solvent interference would be eliminated in the calculation by difference.

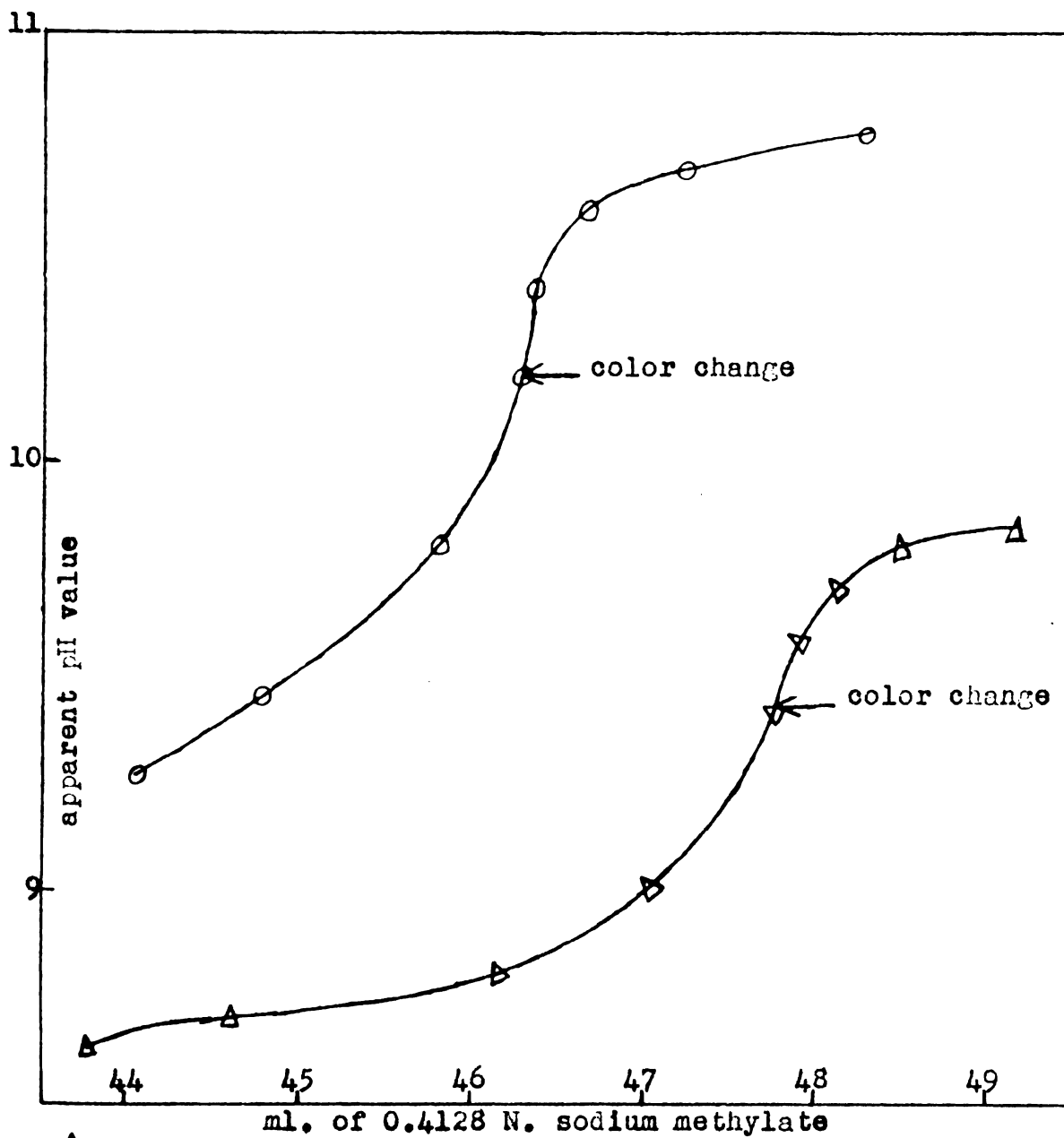
On several trial runs using aliquots of a solution of propionaldehyde in benzene, and a reagent containing acetic anhydride and boron trifluoride etherate in benzene it appeared that consistent results could be attained. It was also apparent that the excess of acetic anhydride need not be as large as when using dioxane as a solvent.

Endpoint Detection:

The solution near the endpoint was of a dark amber color making the phenolphthalein color change at the endpoint difficult to see. Since thymol blue gave a desirable color change, a pH titration was run using a glass electrode to check the applicability of thymol blue as an indicator. The reagent was prepared by pipetting 15 ml. of acetic anhydride and 1 ml. of boron trifluoride etherate into 50 ml. of benzene contained in a 100 ml. volumetric flask. The solution was diluted to 100 ml. with benzene. Ten ml. aliquots were pipetted into 150 ml. beakers and diluted with 20 ml. of benzene. The glass and calomel electrodes were inserted and 4 drops of a 2 % solution of thymol blue in alcohol were added before titration.

To one sample, 3 ml. of dimethylaniline were added to check its effect on the endpoint.





Δ - 10 ml. aliquot of reagent

O - 10 ml. aliquot of reagent plus 3 ml. of dimethylaniline

Figure I

pH Titration of Reagent

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The curves obtained by plotting ml. of standard sodium methylate in methyl alcohol against the apparent pH values and the point at which the indicator changed color are shown in Figure I.

#### A. Determination of Reaction Conditions

An attempt was made to find the best conditions for the reaction. There were many variables which might effect the completeness of reaction. Those considered were reaction time, temperature, concentration of anhydride, concentration of catalyst and the rate of addition of sodium methylate. Because of the thermal instability of the diacetate, and to avoid using pressure bottles it was decided to run the reaction at room temperature. The amount of benzene was kept constant in all determinations.

#### Reagents:

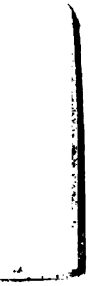
Sodium methylate was prepared by adding 110 g. of C.P. sodium methylate powder to 4 liters of absolute methyl alcohol. The resulting solution was standardized using phenolphthalein indicator against potassium acid phthalate which was dried, weighed and dissolved in water.

Reagents were prepared by pipetting the calculated amounts of acetic anhydride and boron trifluoride etherate into 150 ml. of benzene in a 200 ml. volumetric glass stoppered flask, and diluting with benzene to 200 ml.

#### Procedure:

Twenty ml. of reagent were added to a 250 ml. iodine

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flask containing samples of propionaldehyde weighed in small glass ampoules. Blanks were prepared in a similar manner. The flasks containing samples were chilled in ice for 10 minutes. The ampoules were then broken by means of a detachable glass tamper. The tamper portion was left in the flask which was immediately stoppered and placed on the shaker. After shaking for the desired time, the flasks were removed, and the sides rinsed down with 20 ml. of benzene. Four drops of thymol blue indicator (in absolute alcohol) were added, a small motor driven glass stirrer was inserted, and the solution was titrated with standard sodium methylate to a yellow to blue color change. The difference in equivalents of sodium methylate consumed by the blank and that consumed by the sample was assumed to be equal to the equivalents of aldehyde present. A pre-titration value of the acid content of the sample should be subtracted from the blank value. Table III gives a summary of a series of experiments designed to determine the optimum conditions for the method. The concentrations of acetic anhydride and boron trifluoride etherate are expressed in ml. per millimole of aldehyde.

The endpoints observed using thymol blue were discernable but faded rapidly. A preliminary titration of a solution of acetic anhydride in benzene with no boron trifluoride present gave a sharp stable endpoint with thymol blue indicator.

Assuming that the influence on the endpoint was due to

Table III

Weight of sample in grams	Reagent:		ml. acetic anhydride per millimole of aldehyde	BF <sub>3</sub> etherate per millimole of aldehyde	Rate of addition of sodium methylate	Reaction time	Percent aldehyde calculated
	10 ml. aliquot contains:	acetic anhydride					
0.2494	0.5 ml.	0.1 ml.	0.12 ml.	0.023 ml.	5 ml./min.	1 hour	50.1 %
0.1581	1.0 ml.	0.1 ml.	0.38 ml.	0.037 ml.	5 ml./min.	1 hour	68.9 %
0.1432	1.5 ml.	0.1 ml.	0.62 ml.	0.042 ml.	5 ml./min.	1 hour	73.5 %
0.1837	2.0 ml.	0.1 ml.	0.63 ml.	0.031 ml.	5 ml./min.	1 hour	80.1 %
0.0896	1.5 ml.	0.05 ml.	0.97 ml.	0.032 ml.	5 ml./min.	1 hour	53.9 %
0.0918	1.5 ml.	0.1 ml.	0.94 ml.	0.063 ml.	5 ml./min.	1 hour	60.6 %
0.1022	1.5 ml.	0.2 ml.	0.84 ml.	0.113 ml.	5 ml./min.	1 hour	89.9 %
0.1212	1.5 ml.	0.15 ml.	0.71 ml.	0.071 ml.	3 ml./min.	1 hour	81.7 %
0.0862	1.5 ml.	0.15 ml.	1.00 ml.	0.100 ml.	5 ml./min.	1 hour	56.7 %
0.0753	1.5 ml.	0.15 ml.	1.16 ml.	0.116 ml.	8 ml./min.	1 hour	64.6 %
0.0566	1.5 ml.	0.15 ml.	1.54 ml.	0.154 ml.	3 ml./min.	1 hour	67.2 %
0.0792	1.5 ml.	0.15 ml.	1.10 ml.	0.110 ml.	3 ml./min.	1 hour	63.9 %
0.0601	1.5 ml.	0.15 ml.	1.45 ml.	0.145 ml.	3 ml./min.	2 hours	86.2 %
0.1016	1.5 ml.	0.15 ml.	0.86 ml.	0.086 ml.	3 ml./min.	3 hours	84.4 %

Reaction Variables



the presence of the boron trifluoride, a study was made of the effect of various amounts of boron trifluoride on the endpoint. Dimethylaniline has been used to recover boron trifluoride from reaction liquids containing it (12). It appeared that the co-ordinating power of an excess of dimethylaniline might inhibit the influence of boron trifluoride on the endpoint. Because dimethylaniline is a tertiary amine, it would not consume acetic anhydride and interfere with the determination.

Table IV shows the influence of boron trifluoride on the endpoint and the inhibiting effect of dimethylaniline. The reagent was prepared by pipetting 20 ml. of acetic anhydride into 100 ml. of benzene in a 200 ml. volumetric flask. The solution was then diluted to 200 ml. with benzene. A 10 ml. aliquot of this reagent was used for each titration. Each aliquot was titrated with 0.5050 N. sodium methylate to a thymol blue endpoint.

Table IV

10 ml. aliquot of reagent	Addition to aliquot		ml. of 0.5050 Normal sodium methylate required	Stability of endpoint
	ml. of BF <sub>3</sub> etherate	ml. of dimethyl- aniline		
1			21.45	stable
2			21.40	stable
3	0.1		26.55	35 sec.
4	0.2		29.37	25. sec.
5	0.3		30.07	25 sec.
6	0.2	1.0	27.26	25 sec.
7	0.2	2.0	25.20	25 sec.
8	0.2	3.0	24.03	40 sec.
9	0.2	4.0	24.13	40 sec.
10	0.2	6.0	23.95	40 sec.
11	0.2	8.0	24.10	40 sec.
12	0.2	9.0	23.95	40 sec.

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### B. Determination of Aldehydes

Using conditions derived from Table I, a series of determinations were carried out to test the accuracy of the method as applied to propionaldehyde. As it was found difficult to obtain and keep pure a sample of propionaldehyde, it was decided to determine the propionaldehyde in a commercial preparation obtained from the stock room. These determinations were checked and compared by running a simultaneous determination by the bisulfite method developed by Siggia and Maxcy (11). Samples for both methods were drawn at the same time into pre-weighed glass ampoules.

The bisulfite procedure developed by Siggia and Maxcy involves the use of excess bisulfite and the determination of the excess by acid-base titration. It has the advantages over other bisulfite methods of overcoming equilibrium difficulties and using more stable reagents. An aliquot of standard sulfuric acid is added to a large excess of sodium sulfite solution just before adding the aldehyde sample, to produce sodium bisulfite in situ. The aldehyde reacts with the bisulfite and the excess bisulfite is titrated with standard alkali. The endpoint is determined most accurately by use of a pH meter. A blank titration was run and the amount of aldehyde present was calculated as the difference between the equivalents of alkali consumed by the blank and that consumed by the sample.

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Determination by alkylidene diacetate formation:

Reagents:

Twenty ml. of redistilled acetic anhydride and 2.0 ml. of technical boron trifluoride etherate (48 % boron trifluoride), were pipetted into 150 ml. of benzene contained in a 200 ml. volumetric flask. The solution was then diluted to 200 ml. with benzene.

Dimethylaniline (C.P.).

Standard sodium methylate in absolute methyl alcohol.

A 1 % solution of thymol blue indicator in absolute ethanol.

Procedure:

Samples containing approximately 2 millimoles of propionaldehyde were weighed in small glass ampoules which were blown from 4 mm. soft glass tubing. The ampoules were placed in 250 ml. iodine flasks, and 20 ml. aliquots of the acetic anhydride-boron trifluoride reagent were added by pipet. The flasks were stoppered and chilled in ice water for about 10 minutes to prevent loss of the volatile propionaldehyde when the ampoules were broken. The ampoules were broken as before with a detachable glass tamper, the flasks immediately stoppered and placed on a gentle shaker for 3 hours. After shaking, the sides of the flasks were rinsed down with 20 ml. of benzene. Four ml. of dimethylaniline were added by pipet, the flasks restoppered and allowed to stand for 5 minutes. Four drops of thymol blue

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indicator were then added, and the solutions were titrated with standard sodium methylate to a yellow to blue color change. Two blanks containing everything but samples of propionaldehyde were carried along in the determination. The percent propionaldehyde was calculated as follows:

$$\frac{(B - S) \times N \times M \times 100}{\text{sample wt.} \times 1000} = \% \text{ aldehyde}$$

In the above equation, B equals the ml. of sodium methylate solution consumed by the blank, S equals the ml. of sodium methylate solution consumed by the sample, N equals the normality of the sodium methylate solution, and M equals the molecular weight of the aldehyde. A pre-titration for acid present in the samples was not carried out for either this or the sodium bisulfite addition method. The results of a determination of propionaldehyde by both methods are shown in Table V.

Table V

Method used	Sample wt. in grams	Grams of propionaldehyde found	% propionaldehyde calculated	Average
Bisulfite addition	1.9187	1.7575	91.6	91.8 ± 0.3%
	1.1497	1.0597	92.1	
Diacetate formation	0.1685	0.1556	92.3	91.8 ± 3.7%
	0.1492	0.1421	95.2	
	0.1232	0.1032	87.8	

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In a trial determination of benzaldehyde using the same conditions as were used for propionaldehyde, it was found that the reaction with benzaldehyde was much slower. It was then decided to apply the method to several different aldehydes using the same procedure as used for propionaldehyde. In cases where the reaction appeared slow, longer reaction times were allowed.

Samples of aldehydes of C.P. grade were obtained from the stock room and were freshly distilled. Only a central portion of the constant boiling fraction was taken in each case, and immediately sealed in small pre-weighed glass ampoules.

Table VI shows typical results obtained from determinations of benzaldehyde, isobutyraldehyde and normal butyraldehyde.

Table VI

Sample	Sample wt. in grams	Reaction time	Grams aldehyde found	% Aldehyde calculated
benzaldehyde	.3193	2.5 hr.	.0928	29.1
	.1659	12.0 hr.	.1205	72.6
	.1886	14.0 hr.	.1487	74.3
isobutyraldehyde	.2475	4.0 hr.	.2130	86.1
	.2951	5.5 hr.	.2929	99.2
	.1498	6.0 hr.	.1558	104.0
	.2969	6.0 hr.	.3020	101.7
n-butyraldehyde	.2006	3.0 hr.	.1846	92.0
	.1313	3.0 hr.	.1188	90.1

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## Discussion

Boron trifluoride is known to catalyze many organic reactions. The boron atom (in boron trifluoride), having only six electrons in its outer shell, has a strong tendency to form co-ordinate covalent bonds with atoms having unshared electron pairs.

Booth and Martin in their monograph on boron trifluoride and its derivatives (10), point out that only eight different elements have been found capable of donating electrons to the boron atom of boron trifluoride. They are found in a small area in the second and third periods of the periodic table.

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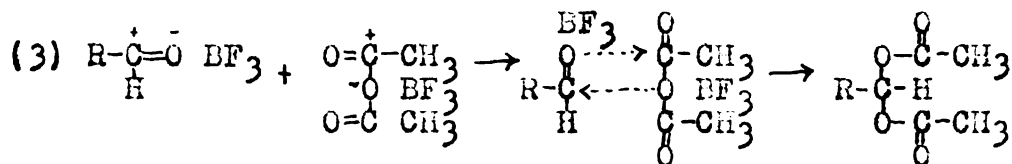
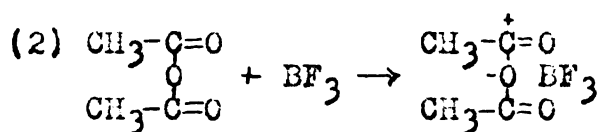
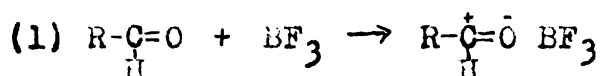
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As boron trifluoride is known to co-ordinate with aldehydes and ketones (10), it may be that it co-ordinates with an enol or resonating form of the carbonyl group.

Boron trifluoride is known to co-ordinate equivalent for equivalent with aldehydes to form complex compounds whose relative stabilities measure the electron donating power of the carbonyl group (13). There appears to be some difference of opinion as to the compound formed when boron trifluoride co-ordinates with acetic anhydride. At approximately the same time in 1931, Bowlus and Nieuwland (14), and Morgan and Taylor (15) reported the compound  $\text{BF}_3 \cdot \text{O}(\text{CH}_3\text{CO})_2$ . Two years

later, Meerwein (16) stated that the compound reported was actually  $[(CH_3CO)_2CHCO]_2O \cdot (BF_3)_3$ .

One possible mechanism of the reaction carried out by Hauser and his co-workers might be proposed on the basis of the ionic structure of the molecules which could be represented when they are co-ordinated with boron trifluoride:



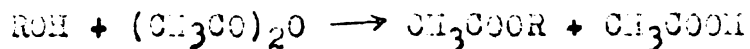
Boron trifluoride is capable of catalyzing many types of organic reactions. These include alkylation, acylation, esterification, condensation, polymerization, and decomposition. Frequently high temperatures and pressures are employed in these reactions. However, only those reactions which might provide an interference or side reaction under the conditions used need to be considered.

All compounds such as alcohols, phenols, and amines which are acetylated by acetic anhydride, will constitute interferences unless a correction can be determined. It is believed that the use of sodium methylate as the titrant will correct for these interferences. A mole of aliphatic alcohol for example, on reaction with a mole of acetic

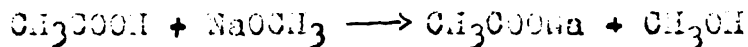
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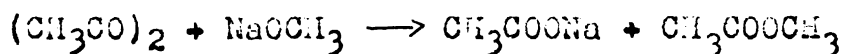
anhydride, forms an ester and acetic acid.



The mole of acetic acid formed consumes one mole of sodium methylate during titration.



If the alcohol were not present, the mole of acetic anhydride would require only one mole of sodium methylate.



When sodium methylate is used, those compounds which react with acetic anhydride liberating a mole of acetic acid for every mole of acetic anhydride consumed, will not constitute an interference provided the amounts are small. If enough of the alcohol, phenol or amine were present to coordinate a considerable amount of the boron trifluoride present, or to consume a considerable part of the acetic anhydride, the reaction between the aldehyde and acetic anhydride may be prevented from going to completion in the reaction time allowed. In such cases, the amounts of acetic anhydride and boron trifluoride would have to be increased.

In general, the reactions catalyzed by boron trifluoride and the variety of conditions used are too numerous for them to be separately considered here. It suffices to say that each sample would have to be considered as to the impurities present, and as to the possibility of interference by them. The monograph by Booth and Martin (10) has an excellent compilation of these reactions, and is adequately supplied

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with references.

The method as applied here to propionaldehyde, appears to compare favorably with the determination by bisulfite addition, although the reproducibility is poor ( $\pm 3\%$ ). A large part of this variance may be due to the fact that samples containing only about 2 millimoles of aldehyde were used. Due to the fading of the endpoint and slight variations in titration rate, the titration values varied about 0.2 ml. for a series of blank titrations. The use of larger samples may greatly increase the accuracy. An increase in the concentration of acetic anhydride would have to accompany such an increase in sample size.

Using the same conditions as were used for the determination of propionaldehyde, the reaction between benzaldehyde and acetic anhydride in the presence of boron trifluoride was very much slower. Of the aldehydes tested, the reactivity in this reaction appears to be:

propionaldehyde > n-butyraldehyde > isobutyraldehyde > benzaldehyde. This tendency might indicate a dependency on the  $\alpha$  hydrogen atom in the aliphatic series, possibly as a rate determining step in the overall reaction. Aromatic aldehydes may proceed by an altogether different path.

The presence of boron trifluoride in the reaction solution complicates the determination of excess acetic anhydride. The yellow to blue endpoint is not sharp and the color rapidly fades back to yellow indicating that the boron

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trifluoride consumes sodium methylate slowly after the endpoint has been reached. One explanation may be that a slow equilibrium between a boron trifluoride-acetic anhydride complex, and the consumption of sodium methylate by boron trifluoride is being established. The addition of an excess of dimethylaniline failed to provide a stable boron trifluoride complex, although the endpoint appeared to be improved. A substance which will complex with boron trifluoride to form a stable compound which is inert toward sodium methylate and acetic anhydride is necessary to provide a more accurate titration.

## SUMMARY

In this work an attempt is made to develop a method for the quantitative determination of aldehydes based on the reaction between aldehydes and acetic anhydride in the presence of boron trifluoride. The method is based on the determination of excess acetic anhydride by titration with sodium methylate.

Benzene was found to be a suitable solvent for the reaction. In the titration of excess acetic anhydride, thymol blue gave a suitable color change at the endpoint.

The addition of dimethyl aniline improved the fading of the endpoint which was due to the presence of boron trifluoride in the reaction mixture.

The reaction when carried out in a benzene solvent appeared slower when higher aldehydes were used. Benzaldehyde requires a much longer reaction time than the lower aliphatic aldehydes.

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