

of the *l*-ester in 25 cc. of dioxane to which 0.5 g. of benzoyl peroxide was added. The solution was placed in the polarimeter cell and heated two hours at 60°, cooled to 25° and read; heated again, etc. The data from this run are given in Table I.

These results are plotted in Curve No. 1, Figs. 1, 2 and 3.

The final reading in each experiment was taken after the cell had been heated overnight in order to determine the rotation of the polymer itself.

In the second experiment on vinyl *l*-butyrate 1.8214 g. of ester and 0.5 g. of benzoyl peroxide in 25 cc. of dioxane were used. The first heating period was forty-five minutes but the change in rotation was so small that the subsequent heating periods were made one hour long. The data for this experiment are collected in Table II and the results are plotted in Curve No. 2 in the Figs. 1, 2 and 3.

The third experiment was made with 1.4914 g.

of ester. The heating periods were ninety minutes long. The results are collected in Table III and Curve No. 3 on Figs. 1, 2 and 3.

Two experiments on *d*-*s*-butyl  $\alpha$ -chloroacrylate were made with 1.663 g. and 1.538 g. of ester, respectively, with 0.5 g. of benzoyl peroxide each in 25 cc. of dioxane. The heating periods were one hour. The final reading in the first experiment was taken after an overnight heating period to give the rotation of the polymer. The results are summarized in Tables IV and V and are plotted in Figs. 4 and 5.

### Summary

*d*-*s*-Butyl  $\alpha$ -chloroacrylate and vinyl *l*- $\beta$ -phenylbutyrate have been prepared and polymerized. The rate of polymerization can be followed conveniently by means of the polariscope. In the presence of peroxides the polymerization of each ester was a first order reaction.

URBANA, ILLINOIS

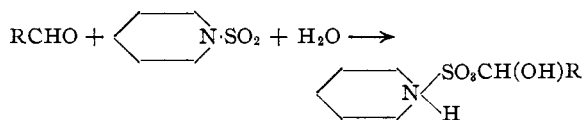
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[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

## Analytical Procedures Employing Karl Fischer Reagent.<sup>1</sup> V. The Determination of Water in the Presence of Carbonyl Compounds

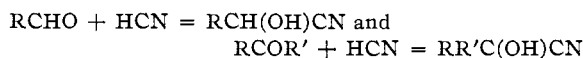
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The usual Karl Fischer reagent is unsatisfactory for the direct titration of water in the presence of aldehydes and ketones due to the tendency to form acetals and ketals,<sup>1</sup> with the production of additional water. A modified reagent containing a minimum quantity of methanol was found satisfactory for water in the presence of ketones but not aldehydes. With aldehydes low results were obtained where appreciable quantities of water were present. It was possible to show that aldehydes react with water and the  $C_6H_5NSO_2$  of the reagent, probably as follows



In the present investigation a procedure was devised by which all types of carbonyl compounds are rendered inert toward the methanol of unmodi-

fied Karl Fischer reagent before the titration for water is started. This is accomplished by the reaction of the carbonyl with a dilute solution of hydrocyanic acid in pyridine (or dioxane)



The resulting cyanhydrin does not interfere with the titration for water.

Inspection of the experimental data of Lapworth and Manske tabulated by Homer Adkins<sup>2</sup> shows that equilibrium in the above reactions favors cyanhydrin formation in most of the cases studied, the conversion usually exceeding 90% for equimolecular mixtures of carbonyl and hydrogen cyanide.

The aldehydes and ketones less reactive toward hydrogen cyanide also show less tendency to combine with the methanol of Karl Fischer reagent, hence the failure of a few carbonyl compounds to form appreciable amounts of the cyanhydrin

(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) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., 1938, p. 807.

TABLE I  
ANALYSES FOR WATER IN CARBONYL COMPOUNDS

Aldehydes	Initial water,	Added	Found	Additional water, wt. %		Added	Found
	wt. % found			Added	Found		
Acetaldehyde	0.12 ± 0.02	4.23	4.26	13.05	13.02		
<i>n</i> -Butyraldehyde	.20 ± 0.02	4.08	4.10	13.05	13.04	21.87	21.86
<i>i</i> -Butyraldehyde <sup>a</sup>	.17 ± 0.02	4.28	4.31	13.06	13.04		
Crotonaldehyde	.44 ± 0.04	4.24	4.28	13.05	13.01		
2-Ethylhexanal-1 <sup>c</sup>	.06 ± 0.03	4.12	4.09	13.02	13.02	21.81	21.84
Benzaldehyde	.15 ± 0.04	4.14	4.10	13.00	12.98	21.78	21.82
Salicylaldehyde	.20 ± 0.01	4.24	4.25	13.05	13.04		
<i>o</i> -Nitrobenzaldehyde	.00 ± 0.03	4.23	4.26	13.04	13.00		
<b>Ketones</b>							
Acetone <sup>b</sup>	0.39 ± 0.02	4.08	4.07	13.05	13.04	21.86	21.89
Ethyl <i>i</i> -propyl <sup>a</sup>	.30 ± 0.06	4.08	4.05	13.00	13.03	21.77	21.83
Di- <i>i</i> -propyl <sup>a</sup>	.10 ± 0.02	4.08	4.05	13.01	13.03	21.77	21.80
Cyclohexanone <sup>a</sup>	.24 ± 0.01	4.14	4.15	13.01	13.01		
Acetophenone	.23 ± 0.00	4.25	4.25	13.00	13.00	21.77	21.77

<sup>a</sup> Du Pont Co. <sup>b</sup> Baker c. p. <sup>c</sup> From the corresponding Carbide and Carbon alcohol; others Eastman Kodak Co.

should not compromise the present analytical scheme.

### Experimental

**Reagents.**—A 2% solution of hydrogen cyanide in pyridine is prepared by adding about 28 ml. of "Carbide and Carbon Co." liquid hydrocyanic acid to 1 liter of Baker c. p. pyridine cooled in a slurry of ice. After thorough mixing the solution is removed and allowed to warm to room temperature. This solution is stable and relatively safe as an analytical reagent (pyridine tends to intensify the odor of hydrogen cyanide; however, the laboratory should be well ventilated).

Karl Fischer reagent is prepared and stored as previously reported.<sup>1</sup>

**Analytical Procedure.**—Fifty to 100 mg. of dry c. p. sodium cyanide and 10 ml. of dry du Pont synthetic methanol are added to a 250 ml. glass stoppered volumetric flask. The flask is then shaken until a homogeneous solution has been obtained. Thirty ml. of 2% hydrogen cyanide in pyridine<sup>3</sup> is added followed by the sample to be titrated for water.<sup>4</sup> The mixture is shaken and allowed to stand for thirty minutes at room temperature after which it is titrated with Karl Fischer reagent. The total titer less that obtained by titrating a blank containing 50 mg. sodium cyanide, 10 ml. methanol and 30 ml. 2% hydrogen cyanide in pyridine, is equivalent to the free water in the sample.

(3) Dioxane can be substituted for pyridine as the hydrogen cyanide solvent, but in this case more sodium cyanide (500 mg.) must be used.

(4) The sample should contain no more than 15 mmoles. of carbonyl, thus allowing about a 25% excess of hydrogen cyanide. This would permit the determination of a minimum of 0.05% water.

### Analytical Results

Analyses for various amounts of water in a group of eight aldehydes and five ketones are given in Table I. The carbonyl compounds, originally containing less than 0.5% of water, were analyzed to determine the exact initial water content. Larger known amounts of water (up to about 22%) were then added and the solutions titrated with Karl Fischer reagent using the titer of the initial carbonyl as a blank. The agreement between water added and recovered is good. With the optimum size sample the usual precision of 0.2 to 0.3% is attained.

Hydrogen cyanide treatment was unnecessary in the case of 37% aqueous formaldehyde (formalin) solution, since no interference was encountered. This substance is exceptional.

### Summary

1. Aldehyde and ketone interference in the Karl Fischer titration for water is inhibited by reaction with an excess of 2% hydrogen cyanide solution in pyridine before titration. The resulting cyanhydrins are inert toward the reagent.

2. Analytical data for eight aldehydes and five ketones of varying water content are reported.

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