

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

Reaction of Esters with Ammonia¹

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Numerous reports appear in the literature on the effect of structural variations on the reactivities of esters. In this connection it seemed of interest to determine the effect on the ease of reaction with ammonia caused by varying the structure of the alcohol radical of the ester. Preliminary experiments showed no reaction between the esters and gaseous ammonia at 100° and under pressures up to 8 atmospheres. Somewhat milder conditions with small amounts of water also present, likewise failed to cause reaction. It was therefore decided to use an aqueous alcohol solution of ammonia as the reagent, although the presence of the water would undoubtedly cause a certain amount of hydrolysis as a side reaction.

Reagents.—The reagent used was a forty per cent. solution (by weight) of alcohol in water, saturated at 25–30° with ammonia.

The *n*- and *i*-butyl acetates were prepared by refluxing one mole of the alcohol with one and one-half moles of the acid. Six cc. of concentrated sulfuric acid per 100 cc. of the mixture was also present. After six to eight hours of refluxing, the esters were washed with water, dried over anhydrous calcium chloride, over potassium carbonate, then fractionated through a 90-cm. column filled with glass rings.

The *s*-butyl acetate was prepared by refluxing a mixture of acetic anhydride and acetic acid with 0.6 cc. of concentrated sulfuric acid per 100 cc. of the mixture. The ester was purified by the process used with the normal ester.

The tertiary butyl acetate was prepared by refluxing equal volumes of the alcohol and acetic anhydride with one gram of zinc dust for a period of ten to twelve hours. The ester was purified in the manner described above. The boiling points and densities at 25° for the esters were as follows: *n*-butyl acetate, 123.7–123.8° at 737 mm., 0.8734; *i*-butyl acetate, 116.1–116.3° at 741 mm., 0.8683; *s*-butyl acetate, 110.4–111.2° at 740 mm., 0.8627; *t*-butyl acetate, 95.3–95.7° at 737 mm., 0.8654.

Procedure.—Two volumetric flasks of 250-cc. capacity were used for each ester. Twenty-five

cc. of ester, measured with a pipet, was placed in each flask, which was then filled to the mark with the aqueous ethyl alcohol solution of ammonia. The reaction mixtures were kept at 25°, and at twenty-four-hour intervals, 50-cc. portions were removed by means of a pipet and diluted with 70 cc. of water. This usually caused the separation of unused ester. In order to remove the excess of ammonia, the solutions were heated to 65–70° on a water-bath and a rapid stream of purified air was bubbled through them till there was no further test with litmus.

The solutions were then diluted to 100 cc. in volumetric flasks and 25-cc. portions were analyzed for ammonium acetate and acetamide in the following manner. Each sample was placed in a Kjeldahl flask, diluted to a volume of 300 cc., and a paste consisting of 2 g. of magnesium oxide in 20 cc. of water was added. The ammonia liberated from the ammonium acetate was distilled into standard acid and the excess acid titrated with 0.1 *N* base. The contents of the Kjeldahl flask were then cooled, again diluted to 300 cc., and 20 cc. of 40% sodium hydroxide solution was added and the solution was boiled. The ammonia liberated by the hydrolysis of the acetamide was distilled into standard acid and determined in the usual manner. This analytical procedure³ gave results on known solutions of acetamide of less than 0.2% error, indicating but little hydrolysis during the distillation with the magnesium oxide. Each determination was made in duplicate from different original reaction mixtures.

When the samples for analysis were diluted with water, unused ester usually separated. As would be expected, the heating to 65° to remove the ammonia caused additional reaction. In order to correct for this, blank determinations were run. Each sample analyzed contained 5 cc. of ester or the reaction products from that amount. Therefore, samples of 5, 3 and 1 cc. would represent the amounts of ester remaining when reaction had proceeded 0, 40 and 80% toward completion. In making the blank determinations, these quantities, 5, 3 and 1 cc. of each ester were dissolved in

(1) Presented at the Kansas City meeting of the American Chemical Society, April, 1936.

(2) This paper is an abstract of the theses submitted by Mr. Johnson and Miss Ratekin in partial fulfillment of the requirements for the degree of Master of Arts at the University of Missouri.

(3) Pucher, Vickery and Leavenworth. *Ind. Eng. Chem., Anal. Ed.*, **7**, 152 (1935).

enough of the original aqueous ethyl alcohol solution of ammonia to make a volume of 50 cc. (the amount always taken for analysis), then diluted with 70 cc. of water, aerated at 65° and analyzed for acetamide and ammonium acetate. The blanks were run in duplicate, and the averages of the results were plotted. The analysis of any sample from a run indicated the extent of reaction and by reference to the graph the necessary correction could be made. Acceptable results could be obtained from this part of the procedure only by a careful control of conditions, such as the size of the openings in the water-bath, rate of the air current, etc.

The results are summarized in the accompanying graphs. With the exception of the *t*-butyl acetate, the reactions of each ester are represented by two pairs of curves. The lower pair represents

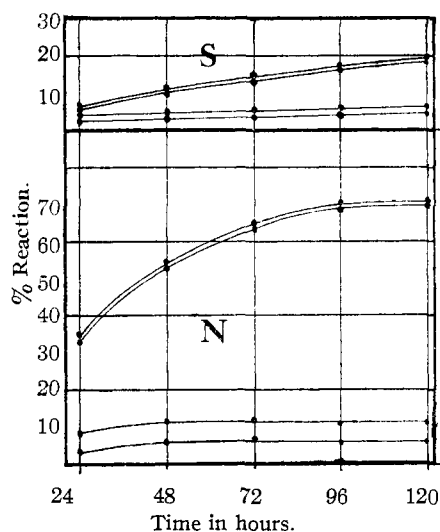


Fig. 1a.—S, *s*-butyl acetate; N, *n*-butyl acetate.

the hydrolysis reaction in each case, and the upper pair the ammonolysis reaction. In any pair of curves, the upper curve corresponds to the total reaction as determined by the analyses. The lower curve is obtained by subtracting the corrections as described above, and represents the reaction taking place at 25°. With the *t*-butyl acetate, the corrections, which are not shown on the graph, were of the same order of magnitude as those for the *s*-butyl ester. Each point on each curve is an average of two determinations made

from different reaction mixtures, rather than from two samples of the same reaction mixture. The agreement among the check determinations was good, showing a variation in two-thirds of the cases of less than 0.5%. The products from the reactions at 25° from the different esters were distributed as indicated in the table.

TABLE I
REACTION PRODUCTS FORMED AT 25°

Ester	Hours	% yield amide	% yield salt	Ratio amide : salt ^a
<i>n</i> -Butyl acetate	120	69.7	6.1	11.4:1
Isobutyl acetate	120	68.8	7.7	8.9:1
<i>s</i> -Butyl acetate	120	18.6	4.8	3.8:1
<i>t</i> -Butyl acetate	360	2.9	2.1	1.4:1

^a These were the ratios at the end of the reaction period.

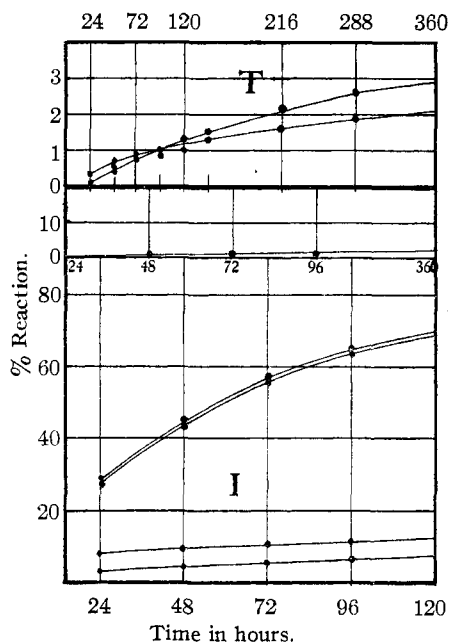


Fig. 1b.—T, *t*-butyl acetate; I, *i*-butyl acetate.

Summary

1. The action of aqueous ethyl alcohol solutions of ammonia on the four butyl acetates was studied.
2. The relative reactivities of the primary, secondary and tertiary butyl acetates toward ammonia was found to be of the order of 24:6:1.
3. A certain amount of hydrolysis took place in each reaction, and increased in importance with the secondary and tertiary butyl acetates.