

ART. XVII.—*The Preparation of Formamide from Ethyl Formate and Ammonium Hydroxide*; by I. K. PHELPS and C. D. DEMING.

[Contributions from the Kent Chemical Laboratory of Yale University—clxi.]

THE action of ammonia on an ester is a typical method for the formation of an acid amide. Hofmann* states that this reaction is particularly easy when the ester itself is somewhat soluble in water; but that in the case of ethyl formate and aqueous ammonia, when allowed to stand at the ordinary temperature, a considerable part of the acid amide is hydrated to ammonium formate, and the amount of acid amide formed is accordingly diminished. He further states that this hydration goes on to such an extent that a yield much in excess of 70 per cent is impossible.

The work given here records the results of experiments which show that such hydration during reaction may be avoided and the formamide may be obtained in amount equal to that indicated by the theory for the action from ethyl formate and ammonia.

Ethyl formate for use in this work was prepared by treating commercial sodium formate with a mixture of absolute alcohol and concentrated sulphuric acid. The crude product obtained as a distillate was fractioned and portions found to boil between 53° and 56° were treated with fused calcium chloride to remove water and alcohol, and redistilled after filtering from the calcium chloride. This distillate was then treated with dry ammonia gas obtained by boiling concentrated ammonium hydroxide in a flask connected with a return condenser and leading the ammonia gas obtained in this way through a lime tower. The ammonium formate precipitated was separated by filtration, and then, by fractional distillation, pure ethyl formate distilling within two-tenths of a degree was obtained free from ammonia gas or other impurity.

In all the experiments recorded in the table definite weights of the pure ethyl formate, chilled in an ice and salt mixture, were treated with ammonium hydroxide of known strength similarly chilled, and the temperature of the mass was not allowed to rise above 0° until after the reaction between the formate and the ammonia solution had been largely completed. The formamide produced in each case was obtained by separating from impurities by fractioning in vacuo in the usual way and distilling the residue after the low-boiling impurities, largely ammonia, ethyl formate, alcohol, and water, had been removed.

* Berichte, xv, 977.

In certain experiments the ethyl formate and ammonium hydroxide were mixed in a 250^{cm}³ distilling flask and the mixture was fractioned in vacuo as soon as it had become homogeneous. In this process the 250^{cm}³ distilling flask containing the mixture was connected to a 100^{cm}³ distilling flask used as a receiver and the formamide was separated from low-boiling impurities by fractioning in vacuo in the usual way, the distilling flask being heated in a water bath at 60° for fifteen minutes after the pressure on the manometer registered 15^{mm}. The formamide was then distilled over, by heating the distilling flask in a bath of sulphuric acid and potassium sulphate,* and caught in the receiver chilled by a current of cold water.

In other experiments the distillation was not made as soon as the ethyl formate and ammonium hydroxide had become homogeneous. In each of these experiments a definite weight of ethyl formate held in a 250^{cm}³ glass-stoppered reagent bottle was treated with pure, commercial ammonium hydroxide of known strength, after chilling each in a mixture of ice and salt, slowly enough so that at no time during mixing did the temperature of the mixture rise above 0°. The mixture at this time consisting of two layers became homogeneous in about five minutes, but was allowed to stand in the ice mixture for fifteen minutes; for the heat given out showed that the reaction progressed after the mass had become homogeneous. This solution was kept tightly stoppered for a definite

No.	Ethyl formate grm.	Ammonium hydroxide Sp. gr. '90 cm ³ .	Time of standing		Formamide	
			hr.	min.	Theory grm.	Found grm.
			A			
(1)	50	30	4	30	30·41	19·06
(2)	50	30	240		30·41	23·40
(3)	50	50			30·41	23·57
(4)	50	50			30·41	22·60
(5)	50	50	1		30·41	28·08
(6)	50	50	1		30·41	27·40
(7)	50	50	2		30·41	29·33
(8)	50	50	2		30·41	29·78
(9)	50	50	2		30·41	29·80
(10)	50	50	5		30·41	30·48
(11)	50	50	5		30·41	30·45
(12)	50	50	6	30	30·41	30·50

B

Treatment with NH₄OH and saturation of mixture with NH₃.

(13)	50	10	4		30·41	30·45
(14)	50	10	4		30·41	30·00
(15)	50	20	4		30·41	30·25

time, after which it was transferred to a 250^{cm}³ distilling flask connected to a 100^{cm}³ distilling flask used as a receiver with the

* H. Seudder, Jour. Am. Chem. Soc., xxv, 161.

use of the least amount of alcohol to remove the last traces from the side-walls of the bottle. The formamide was separated from low-boiling impurities by fractioning in vacuo in the manner described, and the formamide distilled and weighed.

It is obvious from the work recorded in the table that three factors are of influence in the quantitative formation of formamide by the interaction in the cold of ethyl formate and ammonium hydroxide,—the excess of the ammonium hydroxide present, the concentration of the ammonia in the solution, and the time during which the interaction of the two is allowed. From experiments (1) and (2) of section A of the table it is clear that with fixed amounts of ethyl formate and ammonium hydroxide an increase in the length of the time of the reaction is decidedly advantageous. The comparison of experiments (1) and (2) with experiments (5) to (12) shows that increasing the amount of ammonium hydroxide gives a yield in excess of that found with the smaller proportion of ammonium hydroxide. A comparison of experiments (5) to (12) with one another further emphasizes the point that length of time allowed for the completion of the reaction after the mixture has been kept cool during the first of the reaction long enough to prevent hydration is an important factor. It is clear that it is easily possible to obtain the theoretical amount of amide by allowing the mixture to stand five hours or longer. Two hours standing is not quite sufficient.

In section B of the table the results shown were obtained by saturating in the cold, at -10° to 0° for about four hours, the ethyl formate and ammonium hydroxide chilled before mixing in a stoppered reagent bottle fitted with a rubber stopper carrying in one perforation a thermometer dipping into the mixture and in the other the delivery tube for the ammonia gas. This mixture on fractioning in vacuo as described above and distilling the formamide left in the distilling flask gave the theoretical amount of formamide.

An experiment showed that a definite weight of formamide and water when fractioned in vacuo as in the process outlined gave an amount of formamide differing from that taken by less than 0.05 gm.

It is evident that it is possible to obtain from ethyl formate by the action of ammonium hydroxide the theoretical amount of formamide. This may be accomplished by treating the chilled ethyl formate with small amounts of chilled ammonium hydroxide and saturating for some hours in the cold with dry ammonia gas; or, more easily, by treating chilled ethyl formate with larger proportions of chilled ammonium hydroxide and allowing the mixture to stand some hours before distilling in vacuo. The essential thing in the operation is to keep the mixture of the ethyl formate and the ammonium hydroxide at a temperature so low that ammonium formate is not a product of the action.