

diminished pressure. The following fractions were made: (1) 120–180° at 20 mm.; (2) 180–220° at 15 mm.; (3) 220–290°; (4) 290–320°, (5) above 320°. The first 3 fractions were systematically fractionated at 15 mm., and 2 main fractions collected: (1) 170–190°; (2) 190–196°. The boiling point of cetyl alcohol at this pressure is 189.5°. The latter fraction melted at 49–51° after one recrystallization from alcohol.

*Analysis.* Calc. for  $C_{16}H_{34}O$ : C, 79.3; H, 14.0. Found: C, 79.9; H, 13.45.

This material is apparently impure cetyl alcohol. Repeated recrystallization from alcohol tended to separate an alcohol agreeing well with the composition of octodecyl alcohol.

*Analysis.* Calc. for  $C_{18}H_{38}O$ : C, 80.0; H, 14.1. Found: C, 80.1; H, 13.7.

### Summary

The unsaponifiable fraction of ragweed pollen has been systematically examined, and found to contain the following substances: (1) "am-brosterol," a new phytosterol  $C_{20}H_{34}O$  melting at 147–149° (the corresponding acetate melted at 112–113°), (2) a phytosterol,  $C_{27}H_{46}O$ , (3) cetyl alcohol, (4) octodecyl alcohol, (5) traces of hydrocarbon. Some evidence has been obtained indicating the presence of an hydroxyphytosterol.

The writer is indebted to Mr. Merrill C. Hart and Mr. Clayre Pomeroy for the analytical work.

KALAMAZOO, MICHIGAN

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

## CATALYSIS OF THE FORMATION AND HYDROLYSIS OF ACETAMIDE BY ACETIC ACID<sup>1</sup>

BY WILLIAM A. NOYES AND WALTER F. GOEBEL

Received June 2, 1922

In 1884 Menschutkin<sup>2</sup> studied the formation of several amides by heating ammonium acetate and other ammonium salts of organic acids in sealed tubes at various temperatures. He determined the amount of amide formed in 1 hour at various temperatures, and called this the "initial velocity" of the reaction. It is evident that such an expression is very inaccurate, since the amounts formed varied from 6.33% at 125° to 82.83% at 212.5°. He also determined the "limit" of the reaction, that is, the amount of amide formed when the reactions for the formation and hydrolysis of the amide are in equilibrium. Ostwald<sup>3</sup> also studied the hydrolysis of acetamide by different acids. His work was chiefly of interest in determining the "strength" of the acids, before the modern theory of ionization was developed. So far as we are aware, no other studies of the velocities of formation and hydrolysis of amides have been made.

<sup>1</sup> A part of the results given in this article was made the basis for a thesis presented to the Graduate Faculty of the University of Illinois by Walter F. Goebel in partial fulfillment of the requirements for the degree of Master of Arts.

<sup>2</sup> Menschutkin, *J. prakt. Chem.*, **29**, 422 (1844).

<sup>3</sup> Ostwald, *ibid.*, **27**, 1 (1883).

Rosanoff, Gulick and Larkin<sup>4</sup> have shown that acetamide may be prepared by heating ammonium acetate with 1.5 mols of glacial acetic acid for 5 hours in a flask connected with a reflux condenser and then distilling the mixture. They considered that the acetic acid catalyzes the reaction but, so far as their experiments went, it might merely have served to retain the ammonia which escapes when ammonium acetate is heated. The experiments here described were undertaken to determine whether or not the acetic acid actually catalyzes the reaction. The hydrolysis of the amide has also been studied and the results throw an interesting light on the mechanism of these reactions.

Ammonium acetate was prepared partly by crystallizing from alcohol containing an excess of ammonia and allowing the product to stand for some time over sticks of potassium hydroxide in an atmosphere of ammonia, partly by applying the latter treatment directly to a good quality of commercial ammonium acetate. Analyses of different samples gave from 99 to 99.7% of the theoretical amount of ammonia. *Acetamide* was prepared by crystallizing from chloroform or by drying a distilled product on a warm radiator.

**Conditions for the Experiments.**—About 1 g. of ammonium acetate or 0.75–0.80 g. of acetamide was placed in a glass tube 1 cm. in diameter and about 10 cm. long. The other substances were added in nearly accurate molecular proportions, as given in the table and the tube was heated in the vapor of boiling xylene or, in a few cases, in boiling anisole. In xylene the temperature varied a few tenths of a degree from 137°, and in anisole, from 152.5°, depending chiefly on the barometric pressure. The differences found for the speed of the reactions under the conditions chiefly studied were great enough so that differences caused by variations in the temperature were not important. After heating, the tube was cooled by immersing it for a few seconds in boiling water, then in water at 60° and in cold water.

**Analysis.**—The ammonium acetate and acetamide remaining after heating were determined by Folin's method.

The contents of the tube were diluted to about 35 cc. and 5 or 7 g. of dry sodium carbonate was added, the larger quantity being used for the experiments with 1.5 mols of acetic acid. The ammonia was then swept by a rapid current of air into a bottle containing standard hydrochloric acid, and the current of air continued for 2 hours. The solution containing the acetamide was then transferred to a flask, a solution containing about 3.3 g. of sodium hydroxide added and the flask connected with a condenser by means of a Hopkins distilling bulb, as usual for the determination of ammonia. The solution was boiled *without distilling* for a half hour or longer, to saponify the amide. If distilled at once, a considerable amount of the acetamide may go over with the water vapor. The ammonia was collected in standard acid and titrated, as usual.

The following account of one of the experiments illustrates the procedure followed.

A tube containing 0.7925 g. of acetamide (13.43 mols), 0.2411 g. of water (13.39 mols) and 0.0929 g. of acetic acid (0.115 mols) was heated in the vapor of xylene for

<sup>4</sup> Rosanoff, Gulick and Larkin, *THIS JOURNAL*, **33**, 974 (1911).

180 minutes. The contents of the tube were diluted to 35 cc., 5 g. of sodium carbonate was added and the ammonia of the ammonium acetate formed was swept into standard acid by a rapid current of air, passed for 2 hours. The ammonia obtained in this way neutralized 8.26 cc. of 0.1 *N* hydrochloric acid, equivalent to 0.83 mol.; hence 6.15% of the acetamide was hydrolyzed. The solution from which the ammonia of the ammonium acetate had been removed was then distilled, after adding a solution containing 3.3 g. of sodium hydroxide. The distillate neutralized 124.5 cc. of 0.1 *N* hydrochloric acid, equivalent to 12.45 mols of acetamide. The loss was 0.15 mol or 1.12%.

The sum of the ammonia found in the two forms was usually from 1 to 2.5% less than that calculated for the amount of ammonium acetate or acetamide taken. The results are amply accurate, however, for the purposes of this study.

**Equilibrium.**—Menschutkin<sup>2</sup> determined the point of equilibrium between the formation of acetamide and its hydrolysis by prolonged heating. We have determined it by approaching the equilibrium from both sides by heating for 40 or 50 hours at 137°. For acetamide and water without the addition of acid, a mixture containing 0.2 mol of ammonium acetate, 0.8 mol of acetamide and 0.8 mol of water was heated for 40 hours. The ammonium acetate was added because the reaction on that side is autocatalytic and very slow at first. At the end of 40 hours the amount of ammonium acetate differed by only 0.16% from that found in a tube containing ammonium acetate at the start and heated for 50 hours. The point of equilibrium was calculated by adding  $\frac{1}{4}$  of the difference to the percentage of ammonium acetate found in the experiment with acetamide. See the tables.

**Speeds of the Reaction.**—In the following tables the initial speeds of the reactions,  $S_1$  for the formation of acetamide from ammonium acetate,

TABLE I  
SPEED OF FORMATION OF ACETAMIDE FROM AMMONIUM ACETATE AT 137°

Time Minutes	Am. acetate alone	$S_1$	Am. acetate 0.1 mol of acetic acid	$S_1$	Am. acetate 1.5 mol of acetic acid	$S_1$
	Acetamide %		Acetamide %		Acetamide %	
30	9.11	0.0032	...	....	19.45	0.0075
60	17.14	0.0032	21.82	0.0044	32.95	0.0073
120	28.83	0.0030	34.71	0.0038	49.02	0.0066
260	45.66	0.0027	53.83	0.0034	68.70	0.0066
1440	65.40	0.0012	67.34	0.0014	...	....
2400	...	....	77.67	....	...	....
3000	76.93	....	...	....	75.71	....
Equilibrium	77.05	....	78.55	....	75.50	....

and  $S_2$  for the hydrolysis of acetamide to ammonium acetate, were calculated by the formula  $S = Eq \times \left( 2.3 \log \frac{Eq}{Eq-a} \right) \div t$ , in which  $S$  is the fraction of acetamide formed or hydrolyzed during the first minute;

$E_q$  is the fraction of acetamide or ammonium acetate at equilibrium, and  $a$  is the fraction of acetamide or of ammonium acetate formed in the time,  $t$ .

Calculations of the speed by the approximate dimolecular formula  $S = 1/t \times x/A(A - x)$ , or by a graphical method based on the average speeds for successive intervals, give approximately the same values for the initial speeds, which are of most importance for the discussion of the character of the reactions.

TABLE II

SPEED OF FORMATION OF AMMONIUM ACETATE FROM ACETAMIDE AND WATER AT 137°

Time Minutes	Acetamide 1.0 mol H <sub>2</sub> O		Acetamide 1.0 mol H <sub>2</sub> O 0.1 mol acetic acid		Acetamide 1.0 mol H <sub>2</sub> O 1.5 mol acetic acid	
	Am. acetate	$S_2$	Am. acetate	$S_2$	Am. acetate	$S_2$
	%		%		%	
60	0.33	..	2.03	0.00036	9.27	0.0018
180	0.33	..	6.15	0.00040	18.83	0.0020
300	...	..	8.82	0.00038	22.91	0.0020
600	0.53	..	14.97	0.00043	24.50	....
1440	2.64	..	...	.....	...	....
2400	...	..	21.21	.....	...	....
3000	10.16	..	...	.....	...	....
3600	13.61	..	...	.....	...	....
Equilibrium	22.95	..	21.45	.....	24.50	....

About 30 other experiments were made, partly at 152.5°, but mostly at 137°, with the addition of various substances. Some of the results may be mentioned but it seems unnecessary to give details.

At 152.5° the speed of the formation of acetamide is about thrice the speed at 137°. The hydrolysis of acetamide by water shows the same marked autocatalysis as at 137°; 1% is hydrolyzed in about 4½ hours; 3.3% in 6 hours and 8.8% in 14½ hours. Sodium acetate (0.1 mol), ammonia (0.01 or 0.5 mol), alcohol (0.22 mol), ammonium hydrogen carbonate (0.05 mol) or sodium hydroxide (0.03 mol) produce only small effects, except that the last removes an equivalent amount of the acetate radical from the reaction. Sodium hydroxide (0.07 mol) hydrolyzed the equivalent amount of acetamide in 20 minutes, but no further hydrolysis seemed to occur in 6 hours. Hydrochloric acid (0.1 mol) caused the hydrolysis of somewhat more than the equivalent amount of acetamide in 30 minutes, while in 5 hours the amount had increased to 8.5% beyond the equivalent of the hydrochloric acid, agreeing well with the hydrolysis in the presence of 0.1 mol of acetic acid. See Table II.

Menschutkin's results<sup>5</sup> are given in the following table and the speed

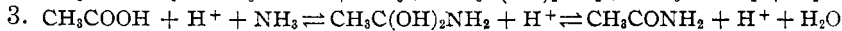
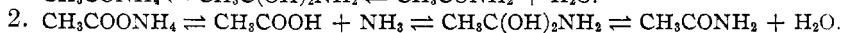
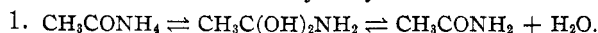
<sup>5</sup> Ref. 2, p. 445.

of reaction has been calculated by the formula given above. Our results at 137° and at 152.5° are included for comparison.

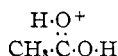
TABLE III  
SPEED OF FORMATION OF ACETAMIDE FROM AMMONIUM ACETATE

Temperature °C.	Acetamide in 1 hr.	Acetamide at equilibrium	Menschutkin S <sub>1</sub>
125	6.33	75.10	0.0011
137	17.14	77.05	0.0032
140	21.36	78.18	0.0042
152.5	44.07	79.00	0.011
155	50.90	81.46	0.013
182.5	78.31	82.82	0.040
212.5	82.83	84.04	....

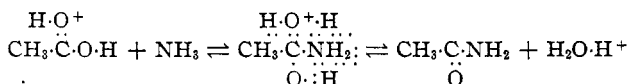
**Discussion.**—Five different equations may be given as an interpretation of the formation and hydrolysis of acetamide.



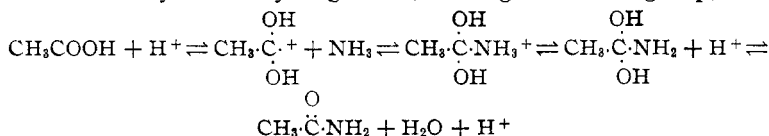
4. Professor Stieglitz, who has been kind enough to read this paper and who has made a number of very helpful suggestions, suggests that the first step in the reaction may be the formation of an oxonium ion,



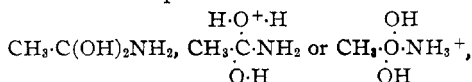
which is very reactive, taking up ammonia and splitting off the oxonium ion of water.



5. The first step might be the addition of a hydrogen ion to the carbonyl oxygen, followed by the addition of ammonia to the liberated positive valence of the carbon, forming an ammonium complex, which would immediately lose a hydrogen ion, leaving the amide group, —NH<sub>2</sub>.



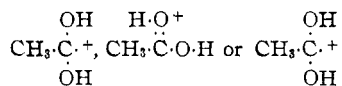
This might be considered as a more detailed development of Reaction 3. Assuming that the decomposition of the intermediate compounds



is very rapid but much more rapid toward the formation of acetamide and water than toward the formation of acetic acid and ammonia, Reaction

1 is mono-molecular toward the right and dimolecular toward the left; Reaction 2 is dimolecular in both directions; Reactions 3, 4 and 5 are either dimolecular reactions catalyzed by hydrogen ions or dimolecular reactions in which hydrogen ions are one of the two reacting substances on both sides.

If the role of the hydrogen ions is simply catalytic,<sup>6</sup> we must suppose that the addition of hydrogen ions to form the intermediate compounds,



is rapid and that the limiting factor in the rate of the reaction is the action of ammonia or water on these intermediate compounds in Reactions 3, 4 and 5. In this case Reactions 2, 3, 4 and 5 are all dimolecular between ammonia and acetic acid in one direction and between acetamide and water in the other. This will be true, both in the experiments in which acetic acid was added and in those in which it was not used.

If the rate of addition of hydrogen ions is the limiting factor and the resulting intermediate compounds react rapidly with ammonia or water, Reactions 3, 4 and 5 will be dimolecular toward the right, with the hydrogen-ion concentration decreasing rapidly as acetamide is formed in the experiments with ammonium acetate alone or with ammonium acetate to which only 0.1 mol acetic acid was added, but it will be dimolecular with one constituent practically constant, in the experiments in which 1.5 mol acetic acid was added. In the opposite direction the reaction between acetamide and water should be dimolecular, but very slow at first when only the hydrogen ions of water are present. The reaction should be autocatalytic, however, and the rate should increase as acetic acid is formed by the dissociation of the ammonium acetate produced. With 0.1 mol of acetic acid the reaction might still be somewhat autocatalytic and also dimolecular, with the hydrogen ion increasing slowly. With 1.5 mol acetic acid the reaction should be dimolecular, with one of the constituents, hydrogen ion, practically constant.

From the concentrations of the reacting substances at equilibrium and the initial speeds of the reactions it is possible to calculate the speeds of the reactions at equilibrium. For Equation 1, the molar concentrations at equilibrium for the experiments involving ammonium acetate alone, or acetamide and water, are 0.1296, 0.4352 and 0.4352, respectively.

For Equation 2, assuming a practically complete dissociation of the am-

<sup>6</sup> The definition of catalyst implied here is that of a substance which reacts rapidly to form some intermediate reaction compound and which is split off again in some subsequent action. As Steiglitz has remarked [*Am. Chem. J.*, **39**, 427 (1908)], "*truly catalytic actions (old style) must merge by imperceptible degrees into truly noncatalytic actions (old style) and there is no dividing line possible at any point.*"

monium acetate to acetic acid and ammonia,<sup>7</sup> the concentrations of ammonia, acetic acid, acetamide and water are 0.1148, 0.1148, 0.3852 and 0.3852, respectively.

For Equations 3, 4 and 5, the concentrations will be the same as for 2, and we may assume that the concentration of the hydrogen ion will be very nearly proportional to the concentration of the acetic acid.

In a similar manner the molar concentrations at equilibrium, for the experiments in which 0.1 mol acetic acid was used, are for Equation 1, ammonium acetate 0.12; acetamide and water, each, 0.44. For Equations 2 to 5 they are, ammonia and acetic acid, 0.107; acetamide and water, 0.393.

For Equation 1, for the experiments with 1.5 mol acetic acid the molar concentrations are, ammonium acetate 0.140; acetamide and water, each, 0.430. For Equations 2 to 5, they are, ammonia and acetic acid, each, 0.122; acetamide and water, each, 0.378.

At equilibrium the speeds of the opposing reactions must be equal, and calculations on the basis of the initial speeds and the molar concentrations just given make it possible to choose between some of the equations with a good degree of probability.

For the experiments with acetamide and water without the addition of acid no initial speed can be calculated because the reaction is autocatalytic. The speed of the reaction from 50 to 60 hours is 5 times that for the first 10 hours, although the reaction has already gone half-way to equilibrium. The fact that it is autocatalytic, however, points very strongly to hydrogen ion as one of the limiting factors in the speed of the reaction. This view receives further support below.

If we let  $S_{2eq}$  and  $S_{1eq}$  stand for the opposing speeds at equilibrium, we may calculate these for Equation 1 with 0.1 mol acetic acid as follows.

$$S_{1eq} = 0.0044 \times 0.12 = 0.00053; S_{2eq} = 0.00038 \times (0.44)^2 = 0.000074.$$

For Equations 2, 3 and 4, as dimolecular reactions between ammonia or hydrogen ion and acetic acid on one side and acetamide and water on the other

$$S_{1eq} = 0.0044 \times (0.12)^2 = 0.000063; S_{2eq} = 0.00038 \times (0.44)^2 = 0.000074.$$

For Equations 3, 4 and 5 as dimolecular reactions with one of the constituents (hydrogen ion or acetic acid) remaining constant

$$S_{1eq} = 0.0044 \times 0.107 = 0.00047; S_{2eq} = 0.00038 \times 0.393 = 0.00015.$$

In a similar manner the speeds at equilibrium may be calculated for the experiments with 1.5 mol acetic acid as follows.

For the mono-dimolecular reaction

$$S_{1eq} = 0.0075 \times 0.140 = 0.00105; S_{2eq} = 0.0018 \times (0.430)^2 = 0.00034.$$

<sup>7</sup> That such an assumption is justified seems evident from the fact that even the acid salt,  $\text{CH}_3\text{CO}_2\text{H} \cdot \text{CH}_3\text{CO}_2\text{NH}_4$ , loses ammonia, as is apparent from the odor, when it is heated to the boiling point, which is only a few degrees higher than the temperature of these experiments.

For the dimolecular reactions

$$S_{1eq} = 0.0075 \times (0.122)^2 = 0.00020; S_{2eq} = 0.0018 \times (0.378)^2 = 0.00036.$$

For the dimolecular reactions with one constituent constant

$$S_{1eq} = 0.0075 \times 0.122 = 0.00091; S_{2eq} = 0.0018 \times 0.378 = 0.00070.$$

Examination of these results makes it clear that the mono-dimolecular reactions are excluded in every case. The results with ammonium acetate alone, in which the monomolecular formula for calculating the initial speed fails to give good results after a transformation of 30% has occurred, show that in that case, also, the formation of acetamide is not a monomolecular reaction.

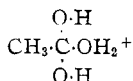
For the experiments with 0.1 mol acetic acid the results agree best for the dimolecular formula in which both constituents change their concentrations as the reaction proceeds. The speeds for the hydrolysis of acetamide, calculated by the monomolecular formula, indicate that the reaction is still slightly autocatalytic and point once more to acetic acid or hydrogen ion as the effective agent in the reaction.

Acetic acid, which must be the other constituent of the dimolecular reaction, probably reacts in one of the active forms produced by the addition of hydrogen ions as supposed in Reactions 3, 4 and 5. Of these, Reactions 3 and 5 seem simpler and more in accord with the formation of aldehyde ammonia and of acetamide by the action of ammonia on acetic ester, a reaction which is almost quantitative and fairly rapid at ordinary temperatures.

In the hydrolysis of acetamide the hydrogen ions of acetic acid are the dominating factor, the speed of the reaction being almost negligible in their absence. Here, again, the supposition that the hydrogen ions combine with acetamide to form the reactive intermediate compound,



brings the reaction into close relationship to the formation of chloral hydrate, the hydrate of oxalic acid,  $(\text{HO})_3\text{C}-\text{C}(\text{OH})_3$ , cyanohydrins, oximes and many other compounds. By supposing that this complex combines



with a mol of water to form the oxonium ion, the analogy with Reaction 5 in the opposite direction is complete and the interpretation is similar to that of Stieglitz.

In the hydrolysis of acetamide by sodium hydroxide it would seem that the sodium ions unite with the oxygen of the carbonyl while hydroxyl unites with the carbon. This is followed by the loss of ammonia and the reverse reaction is almost completely suppressed, probably because am-



monia does not add itself to the carbonyl of the acetate ion,  $\left(\text{CH}_3\overset{\text{O}}{\underset{\cdot\cdot}{\text{C}}}\text{O}\right)^-$  or to the sodium salt. The fact that the hydrolysis of acetamide, either by hydrochloric acid or by sodium hydroxide is rapid at  $100^\circ$  while the hydrolysis by water alone is very slow, may be taken as very strong evidence that the decomposition of the intermediate compound,  $\text{CH}_3\overset{\text{OH}}{\underset{\text{NH}_2}{\text{C}}}\text{OH}$ , is very rapid in comparison with the addition of hydrogen ions and hydroxyl or amide ions.

The enol form of acetic acid,  $\text{CH}_2=\text{C}(\text{OH})_2$ , is probably involved in some of the reactions, since Menshutkin has shown<sup>8</sup> that the ammonium salts of benzoic and anisic acids, which can not pass into the enol form, are converted into the amides very slowly indeed.

For the experiments with 1.5 mol of acetic acid the equations for a dimolecular reaction with one of the constituents constant give the best agreement. Here the monomolecular formula for calculating the initial speed (the same formula may be used for a dimolecular reaction in which one constituent remains constant) gives results which fall off only 12% when 90% of the transformation at equilibrium has occurred.

The conclusion seems justified, therefore, that the formation of acetamide from ammonium acetate alone or in the presence of 0.1 mol acetic acid is a dimolecular reaction with the two constituents of the reaction decreasing as it proceeds. Since the same reaction shows the characteristics of a dimolecular reaction with one constituent constant in the presence of 1.5 mol acetic acid and since, in that case, ammonia is the only constituent which changes steadily in its concentration, it would seem that the two constituents of the dimolecular reaction are ammonia and acetic acid. The ammonia might act as the ammonium ion, as ammonia or as the amide ion,  $\text{NH}_2^-$ . That it does not act as the ammonium ion seems evident from the fact that hydrochloric acid hydrolyzes acetamide rapidly and completely and the ammonium ions formed show no tendency to form acetamide with acetic acid. Professor Stieglitz has pointed out (private communication) that if amide ions were an effective limiting constituent the hydrogen ions, which increase the speed, should have an equal effect in the opposite direction by repressing the ionization of ammonia to amide and hydrogen ions. It would seem, therefore, that ammonia must react as such, either adding directly to a reaction complex (Reaction 5) or separating into amide ion and hydrogen in the immediate presence of some reactive substance,<sup>9</sup> which is formed by the addition of hydrogen ions to acetic acid.

**Preparation of Acetamide.**—Rosanoff, Gulick and Larkin<sup>10</sup> and Hitch

<sup>8</sup> Menshutkin, *J. prakt. Chem.*, **29**, 432, 435 (1884).

<sup>9</sup> W. A. Noyes, *Science*, **20**, 498 (1904).

<sup>10</sup> Ref. 4, p. 975.

and Gilbert<sup>11</sup> have given directions for the preparation of acetamide based on the use of acetic acid and ammonium acetate, or ammonium carbonate, in open flasks, in place of the old, sealed-tube methods. These methods may be further modified to advantage as follows. (1) By using equal mols of ammonium acetate and glacial acetic acid (40 and 30 g.) the mixture may be heated to 140–145° before it begins to boil. (2) If boiled rapidly at first, ammonia will escape, but if heated just short of boiling for 30 to 50 minutes the mixture may then be distilled *slowly* through a good fractioning column and if the temperature is not allowed to go above 103–104° at the top of the column, there will be very little loss of ammonium acetate or acetamide. Ammonium acetate escapes much more easily than does acetamide, if the distillation is too rapid. (3) The removal of water by the distillation shifts the equilibrium toward the formation of acetamide. By very careful distillation a residue of acetamide boiling at 215–217° may be obtained. This is best transferred to a plain distilling bulb for final distillation. The yield may reach 95 to 98% of the theoretical amount for the ammonia of the ammonium acetate used.

### Conclusions

1. Acetic acid catalyzes both the formation of acetamide from ammonium acetate and the hydrolysis of acetamide by water.

2. The hydrolysis of acetamide by water is autocatalytic, doubtless because the acetic acid from the dissociation of the ammonium acetate formed catalyzes the reaction.

3. The formation of acetamide from ammonium acetate with or without the addition of 0.1 mol of acetic acid is essentially a dimolecular reaction between ammonia and acetic acid, probably with the formation of an intermediate compound,  $\text{CH}_3\text{-}\overset{\text{O-H}}{\underset{\text{O-H}}{\text{C}}}\text{-NH}_2$ , as an ephemeral step in the process.

4. The formation and hydrolysis of acetamide in the presence of 1.5 mol of acetic acid is chiefly a dimolecular reaction with one of the constituents, hydrogen ion or acetic acid, constant. The other constituent limiting the speed of the reaction must be ammonia on one side and acetamide on the other.

5. A nearly quantitative method of preparing acetamide is described, dependent on heating a mixture of equal mols of ammonium acetate and acetic acid for a short time, followed by a slow distillation of the water formed and the excess of acetic acid.

URBANA, ILLINOIS

<sup>11</sup> Hitch and Gilbert, *THIS JOURNAL*, **35**, 1780 (1913).