

A STUDY OF THE REACTIONS OF AMMONIUM SULPHAMATE WITH AMIDES AND UREAS¹

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ABSTRACT

The preparation of nitriles from amides and ammonium sulphamate was investigated. The method was found to be generally applicable and good yields were obtained in most cases. The mechanism of the reaction involved the liberation of ammonia and the formation of ammonium N-carbonyl sulphamates, which decomposed into nitriles and ammonium bisulphate.

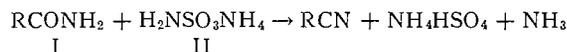
The mechanism for the formation of guanidine and cyanuric acid from ureas was elucidated. The effects of methyl, phenyl, acetyl, and benzoyl groups on the reactivity of the urea molecule were determined. Methylamine and aniline were obtained from methylurea and phenylurea together with guanidine and cyanuric acid. Acetylurea and benzoylurea formed acetonitrile and benzonitrile, the yield of guanidine being low but that of cyanuric acid very high.

INTRODUCTION

AMIDES AND AMMONIUM SULPHAMATE

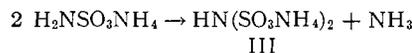
Nitriles had been obtained before from amides by treatment with phosphorus pentachloride, phosphorus pentoxide, phosphorus oxychloride, and thionyl chloride. Short and long chain aliphatic and aromatic amides required the use of different dehydrating agents.

In 1950 Boivin (2) reported that nitriles were formed when simple aliphatic and aromatic amides (1) were heated with ammonium sulphamate (II) at 180–190° C. The reaction proceeded with the evolution of ammonia and the formation of ammonium bisulphate.



In order to determine whether this method of preparing nitriles was generally applicable, a series of amides, including short and long chain aliphatic, aromatic, α -substituted aliphatic, and heterocyclic amides were heated with ammonium sulphamate. The corresponding nitriles were obtained in fairly good yields. They are listed in Table I.

It was known that ammonium sulphamate did not behave as a normal dehydrating agent (3). Berglund (1) found that when heated alone at 170–180° C. it was transformed into ammonium imidodisulphonate (III) and ammonia.



This showed that there was the possibility of the formation of an intermediate when amides were heated with ammonium sulphamate. The possibility was

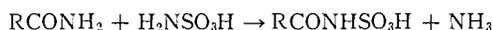
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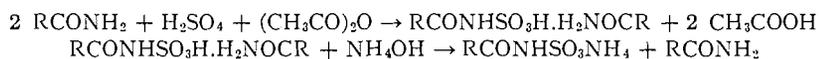
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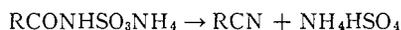
substantiated during the present work. In fact, it was found that mixtures of amides and ammonium sulphamate when heated directly at 200° C. produced nitriles in very low yields. It was necessary to heat the mixtures initially at 150° C. and to raise the temperature slowly to 200° C. Furthermore Cuprey (4) mentioned that amides reacted with sulphamic acid to yield N-carbonyl sulphamic acids.



It thus seemed probable that the intermediate formed during the reaction of amides and ammonium sulphamate was of the ammonium N-carbonyl sulphamate type. In order to prove this unequivocally, seven ammonium N-carbonyl sulphamates were prepared; amides were treated with a solution of sulphuric acid in acetic anhydride and formed the amide salt of amido sulphonic acids, which with ammonium hydroxide formed ammonium N-carbonyl sulphamates.

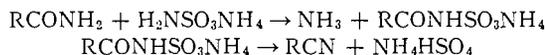


When these ammonium salts were heated at 170–180° C. nitriles and ammonium bisulphate were formed.



The yields of nitriles from ammonium N-carbonyl sulphamates were very good, varying from 90 to 95%. The results are shown in Table II.

Thus the formation of nitriles from amides and ammonium sulphamate involves a condensation of the amide with ammonium sulphamate by liberation of ammonia to yield ammonium N-carbonyl sulphamates, which decompose into nitriles and ammonium bisulphate.



The mechanism indicated that secondary amides, which cannot be readily dehydrated, should produce nitriles and amines when heated with ammonium sulphamate. Three secondary amides, namely, acetanilide, *o*-acetamidobenzoic acid, and *p*-acetamidobenzoic acid were heated with ammonium sulphamate. In each case acetonitrile was isolated together with aniline, *o*-aminobenzoic acid, and *p*-aminobenzoic acid.

UREAS AND AMMONIUM SULPHAMATE

Boivin and Lovecy (3) reported that guanidine was formed when urea was heated with ammonium sulphamate. It was thus of interest to determine the behavior not only of urea but also of mono- and di-substituted ureas towards ammonium sulphamate.

Urea

When urea was heated with ammonium sulphamate, guanidine and cyanuric acid were formed. The yield of guanidine varied with the temperature and time of the reaction but only slightly with the amount of ammonium sulphamate used. The results are given in Table III.

Alkylureas

It was found that methylurea and 1,3-dimethylurea reacted with ammonium sulphamate in a manner analogous to that of urea. Methylamine was isolated from the reaction mixtures.

Methyl groups had little effect on the reactivity of the urea molecule. Guanidine was isolated and not methylguanidine. The yield of guanidine varied with the temperature and time of the reaction and the amount of ammonium sulphamate used. The results are found in Tables IV and V.

Arylureas

Monophenylurea when heated with ammonium sulphamate reacted as did the alkylureas; guanidine and cyanuric acid were formed together with aniline and diphenylurea. The yield of guanidine was affected by the amount of ammonium sulphamate used but only slightly by the temperature and time of the reaction. The results are shown in Table VI.

Diphenylurea produced only aniline and no guanidine nor cyanuric acid when heated with ammonium sulphamate.

Alkoyl and Aroylureas

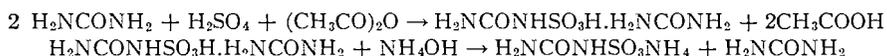
The effects of alkoyl and aroyl groups on the reactivity of the urea molecule were studied. It was noted that the carbonyl of an acetyl or benzoyl group was more reactive than the carbonyl group of urea. In the reactions of acetylurea and benzoylurea with ammonium sulphamate, the substituted urea decomposed to form acetamide or benzamide and hence the corresponding nitriles and cyanuric acid. The yield of guanidine was low while that of cyanuric acid was very high. The results are listed in Tables VII and VIII.

Diacetylurea when heated with ammonium sulphamate produced only acetonitrile and no guanidine nor cyanuric acid.

Salts of Carbamylsulphamate

Boivin and Lovecy (3) reported that ammonium carbamylsulphamate was formed when urea reacted with ammonium sulphamate at 140° C.

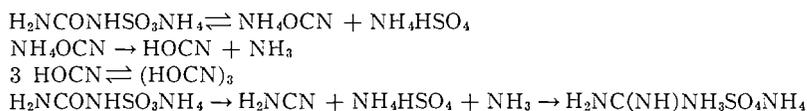
Ammonium carbamylsulphamate was prepared in a manner analogous to the preparation of ammonium N-carbonyl sulphamates previously mentioned. Urea reacted with sulphuric acid in acetic anhydride to form urea carbamylsulphamate. This viscous salt, which could not be induced to crystallize immediately, was treated with ammonium hydroxide to form ammonium carbamylsulphamate.



When ammonium carbamylsulphamate was heated alone, guanidine and cyanuric acid were formed. The yield of guanidine was increased by the addition of ammonium sulphamate. The results are given in Table IX.

By analogy with the reactions of amides and ammonium sulphamate, or of the intermediate ammonium N-carbonyl sulphamates, it seemed that ammonium carbamylsulphamate should produce the corresponding nitrile, which

is cyanamide. It is well known that cyanamide in the presence of an ammonium salt is converted into guanidine or its trimer, melamine. Thus the formation of guanidine from ammonium carbamylsulphamate would proceed as follows.



In order to prove that the formation of guanidine does occur through the condensation of cyanic acid with ammonium sulphamate to form ammonium carbamylsulphamate, potassium, sodium, and urea carbamylsulphamates were heated alone and with ammonium sulphamate.

As expected, only cyanuric acid was isolated when these three salts were heated alone. It was necessary to heat the salts with ammonium sulphamate in order that guanidine be formed.

In view of the experimental results obtained the mechanism of the formation of guanidine occurs through the condensation of cyanic acid with ammonium sulphamate, forming ammonium carbamylsulphamate, which is converted into guanidine.



Salts of N-Methylcarbamylsulphamate

In order to determine why no methylguanidine was formed when methylurea and dimethylurea were heated with ammonium sulphamate, the behavior of ammonium N-methylcarbamylsulphamate was studied.

This salt heated alone produced only cyanuric acid. With ammonium sulphamate at temperatures not exceeding 230° C. methylguanidine together with traces of guanidine was isolated. At temperatures above 230° C. only guanidine and no methylguanidine was formed. The results are listed in Table X.

The fact that methylguanidine was readily formed from ammonium sulphamate and ammonium N-methylcarbamylsulphamate proves that the formation of this salt is an essential step in the production of methylguanidine from methylurea and dimethylurea. However, since methylguanidine is not isolated from the reactions of methylurea and dimethylurea, the formation of ammonium N-methylcarbamylsulphamate was prevented. The experimental conditions used favored the formation of ammonium carbamylsulphamate and hence guanidine.

Thus two opposing reactions were involved when methylurea or dimethylurea was heated with ammonium sulphamate; guanidine was formed in preference to methylguanidine.

From the study it is concluded that the formation of nitriles by the reaction of amides and ammonium sulphamate involves a condensation of the amide with ammonium sulphamate, the liberation of ammonia, and the formation of ammonium N-carbonyl sulphamates, which decompose into nitriles and ammonium bisulphate. This method of preparing nitriles is generally applicable to most amides.

The formation of guanidine from urea and substituted ureas is due to the condensation of cyanic acid with ammonium sulphamate resulting in the formation of ammonium carbamylsulphamate, which is converted into guanidine and ammonium bisulphate. Alkyl and aryl ureas produce amines and alkoyl and aroyl ureas produce nitriles in addition to guanidine and cyanuric acid.

EXPERIMENTAL

Direct Synthesis of Nitriles

In a distilling flask equipped with a short column was placed ammonium sulphamate (17.10 gm., 0.15 mole) and an amide (0.1 mole). The mixture was heated in a metal bath, the temperature of which was slowly raised from 150° C. up to 190–200° C. The liquid nitriles were collected by distillation and the solid ones by vacuum distillation or extraction with a suitable solvent. The results are shown in Table I.

TABLE I
AMIDES AND NITRILES

Amides	Nitriles	M.p., ° C.	B.p., ° C.	Yield, %	Calc., % N	Found, % N
X	CH ₃ CN		81–82	10	34.15	34.20
C ₃ H ₇ CONH ₂	C ₃ H ₇ CN		216	65	20.3	20.38
C ₄ H ₉ CONH ₂	C ₄ H ₉ CN		142	70	16.75	16.80
C ₄ H ₉ CONH ₂	C ₄ H ₉ CN		129–130	80	16.75	16.81
C ₅ H ₁₁ CONH ₂	C ₅ H ₁₁ CN		162	80	14.43	14.38
C ₁₇ H ₃₅ CONH ₂	C ₁₇ H ₃₅ CN	41.5		92	5.28	5.30
C ₄ H ₈ (CONH ₂) ₂	C ₄ H ₈ (CN) ₂		153/6 mm.	45	25.92	25.98
<i>o</i> -CH ₃ C ₆ H ₄ CONH ₂	<i>o</i> -CH ₃ C ₆ H ₄ CN		201–202	75	11.96	12.0
<i>p</i> -CH ₃ C ₆ H ₄ CONH ₂	<i>p</i> -CH ₃ C ₆ H ₄ CN	30	215–216	90	11.96	11.99
HOC ₆ H ₄ CONH ₂	HOC ₆ H ₄ CN	98		25	11.76	11.83
C ₆ H ₅ CH ₂ CONH ₂	C ₆ H ₅ CH ₂ CN		206/107 mm.	45	11.96	11.94
C ₂ H ₅ CH(C ₆ H ₅)CONH ₂	C ₂ H ₅ CH(C ₆ H ₅)CN		107/7 mm.	80	9.65	9.7
C ₆ H ₅ OCH ₂ CONH ₂	C ₆ H ₅ OCH ₂ CN		115/11 mm.	65	10.52	10.58
C ₁₀ H ₇ CH ₂ CONH ₂	C ₁₀ H ₇ CH ₂ CN	33	178/12 mm.	58	8.38	8.40
C ₄ H ₉ OCONH ₂	C ₄ H ₉ OCN		148–150	15	15.05	15.09
C ₅ H ₃ NCONH ₂	C ₅ H ₃ NCN	51		85	26.92	26.99

X = CH₃CONHC₆H₅ or *o*-CH₃CONHC₆H₄COOH or *p*-CH₃CONHC₆H₄COOH.

Preparation of Nitriles from Ammonium N-Carbonyl Sulphamates

An amide (0.1 mole) was added to cold mixture of acetic anhydride (250 ml.) and sulphuric acid (49.0 gm., 0.5 mole). The solution was cooled to –20° C. in an acetone – dry-ice bath. The bulky white solid which separated out was filtered, washed well with anhydrous ethyl ether, and dissolved in ethanol (250 ml.). The alcoholic solution was treated with ammonium hydroxide (80 ml.) and cooled. The ammonium N-carbonyl sulphamates were isolated as crystalline solids which are not described in the literature. The results are shown in Table II.

Upon the heating of these ammonium salts at 170–180° C. nitriles and ammonium bisulphate were isolated. The nitriles isolated from ammonium N-carbonyl sulphamates are given in Table II.

Ureas and Ammonium Sulphamate

The ureas (0.1 mole) and ammonium sulphamate (0.1, 0.2, 0.3 mole) were heated in the same manner as described for the amides and ammonium sulphamate. The temperature and time of the reaction were varied.

The reaction products were water leached and the filtrates were analyzed for guanidine and cyanuric acid. Guanidine was estimated as the picrate and cyanuric acid as melamine cyanurate. The results are listed in Tables III, IV, V, VI, VII, and VIII.

TABLE II
AMMONIUM N-CARBONYL SULPHAMATES AND NITRILES

Ammonium N-carbonyl sulphamates	M.p., °C.	Yield, %	Calc.		Found		Nitriles	Yield, %
			% N	% SO ₃	% N	% SO ₃		
C ₁₇ H ₃₅ CONHSO ₃ NH ₄	115	90	7.37	21.05	7.39	20.98	C ₁₇ H ₃₅ CN	95
C ₁₇ H ₃₅ (CONHSO ₃ NH ₄) ₂	208	85	16.56	47.33	16.48	47.5	C ₁₇ H ₃₅ (CN) ₂	90
C ₇ H ₇ CONHSO ₃ NH ₄	140	95	12.07	34.49	12.0	34.53	C ₇ H ₇ CN	97
C ₇ H ₇ CONHSO ₃ NH ₄	160	75	12.07	34.49	11.99	34.51	C ₇ H ₇ CN	95
HOOC ₆ H ₄ CONHSO ₃ NH ₄	143	80	11.96	34.19	11.91	34.1	HOOC ₆ H ₄ CN	95
C ₆ H ₅ CH ₂ CONHSO ₃ NH ₄	127	95	12.07	34.48	11.99	34.51	C ₆ H ₅ CH ₂ CN	85
C ₁₀ H ₇ CH ₂ CONHSO ₃ NH ₄	157	85	9.93	28.39	9.97	28.43	C ₁₀ H ₇ CH ₂ CN	95

TABLE III
UREA AND AMMONIUM SULPHAMATE

Molar ratio H ₂ NCONH ₂ : H ₂ NSO ₃ NH ₄	Temp., °C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	200	50	45	30.1	32.1
1:1	230	75	70	30.2	3.0
1:2	200	50	45	33.9	2.0
1:2	200	74	70	33.8	4.6
1:2	230	23	15	59.2	14.0
1:2	230	14	8	59.2	4.0
1:2	250	14	5	40.7	16.0
1:2	275	8	4	40.3	14.0
1:3	200	50	45	32.4	1.0
1:3	230	75	70	35.8	4.0

TABLE IV
METHYLUREA AND AMMONIUM SULPHAMATE

Molar ratio CH ₃ NHCONH ₂ : H ₂ NSO ₃ NH ₄	Temp., °C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	250	20	10	Nil	25.6
1:2	200	65	59	8.5	Traces
1:2	210	61	48	25.4	2.3
1:2	220	45	31	27.1	4.2
1:2	230	30	13	27.1	4.2
1:2	250	14	4	28.8	4.9
1:3	250	20	10	32.2	7.0
1:3	250	30	20	49.4	4.2

TABLE V
 DIMETHYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $\text{CH}_3\text{NHCONHCH}_3$: $\text{H}_2\text{NSO}_3\text{NH}_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	250	16	10	2.0	2.3
1:1	250	28	20	2.0	Traces
1:2	200	110	100	1.8	Traces
1:2	220	48	38	2.0	Traces
1:2	230	25	16	11.0	Traces
1:2	230	42	35	25.0	Traces
1:2	250	23	10	29.0	Traces
1:2	250	31	20	29.0	Traces
1:3	250	16	10	35.7	2.3
1:3	250	28	20	35.7	2.3

 TABLE VI
 MONOPHENYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $\text{C}_6\text{H}_5\text{NHCONH}_2$: $\text{H}_2\text{NSO}_3\text{NH}_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:1	230	35	20	12.5	17.0
1:2	200	180	170	Nil	Nil
1:2	230	70	60	24.0	26.0
1:2	250	23	14	24.0	26.0
1:2	275	18	4	25.0	26.5
1:3	250	25	14	30.0	15.0
1:3	275	18	4	50.0	7.0

 TABLE VII
 MONOACETYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $\text{CH}_3\text{CONHCONH}_2$: $\text{H}_2\text{NSO}_3\text{NH}_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid*
1:1	230	60	25	13.0	85.0
1:2	200	120	105	23.7	75.0
1:2	230	60	25	25.1	81.0
1:2	230	75	50	25.4	79.0
1:2	250	30	10	25.1	81.0
1:2	275	45	4	17.0	50.0
1:3	230	60	25	26.2	76.0

*The method of determining cyanuric acid by the use of melamine is known to give high results.

Salts of Carbamylsulphamate

The viscous urea salt was prepared as described by Boivin and Lovecy (3). After decanting, the salt was well washed with anhydrous ethyl ether, dissolved in ethanol (50 ml.), and anhydrous ethyl ether was added (300 ml.). The mixture was left standing overnight at room temperature. The white needle-like solid was filtered, well washed with ether, and dried *in vacuo* for two days. Pure urea carbamylsulphamate was obtained, m.p. 123° C. Yield, 30%.

TABLE VIII
 MONOBENZOYLUREA AND AMMONIUM SULPHAMATE

Molar ratio $C_6H_5CONHCONH_2 : H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid*
1:1	230	45	40	10.0	88.0
1:2	200	150	130	23.0	70.0
1:2	230	50	45	27.0	80.0
1:2	230	45	30	25.0	80.0
1:2	275	18	3	26.0	80.0
1:3	230	45	40	27.0	78.0

*The method of determining cyanuric acid by the use of melamine is known to give high results.

Calculated for $C_2H_7O_5N_4S$: C, 12.06%; H, 3.52%; N, 28.14%; S, 16.08%.
 Found: C, 12.01%; H, 3.5%; N, 28.2%; S, 16.2%.

The ammonium, sodium, and potassium urea carbamylsulphamates were prepared by treating an alcoholic solution of the viscous urea salt with an aqueous solution of the appropriate hydroxide. Ammonium carbamylsulphamate was isolated, m.p. 167–168° C. (reported m.p. 167.5–168° C.). Sodium carbamylsulphamate had no definite melting point but decomposed at 220° C. Yield, 70%. Calculated for $CH_3O_4N_2S Na$: N, 17.28%; SO_3 , 49.38%. Found: N, 17.32%; SO_3 , 49.41%. Potassium carbamylsulphamate had no definite melting point but decomposed at 200° C. Yield, 75%. Calculated for $CH_3O_4N_2SK$: N, 15.73%; SO_3 , 44.90%. Found: N, 15.78%; SO_3 , 44.80%.

The carbamylsulphamates were heated alone and with ammonium sulphamate in the same manner as described for the reactions of amides and ammonium sulphamate. The reaction products were water leached and the filtrates were analyzed for guanidine and cyanuric acid. The results obtained for ammonium carbamylsulphamate are listed in Table IX.

 TABLE IX
 AMMONIUM CARBAMYLSULPHAMATE

Molar ratio $H_2NCONHSO_3NH_4 : H_2NSO_3NH_4$	Temp., ° C.	Time in minutes		Yield, %	
		Total	Above 200° C.	Guanidine	Cyanuric acid
1:0	200	25	20	Nil	50.0
1:0	230	25	20	19.0	70.0
1:0	250	18	10	35.0	35.0
1:1	200	27	20	16.0	25.0
1:1	230	18	10	49.0	11.0
1:2	230	25	20	69.0	14.0
1:2	250	25	20	97.0	2.0
1:4	230	16	10	76.0	7.0
1:4	230	28	20	80.0	7.0

Salts of *N*-Methylcarbamylsulphamate

Methylurea (73.0 gm., 1.0 mole) was added to a cold mixture of acetic anhydride (250 ml.) and sulphuric acid (49.0 gm., 0.5 mole). The solution

was cooled to -20° C. and the viscous methylurea salt was decanted. Crystallization was effected by dissolving the salt in ethanol (150 ml.) and adding anhydrous ethyl ether (100 ml.). The white crystalline methylurea salt was isolated, m.p. $107-108^{\circ}$ C. Yield, 80%. Calculated for $C_4H_{11}O_5N_4S$: N, 24.67%; SO_3 , 35.2%. Found: N, 24.7%; SO_3 , 35.3%.

Ammonium N-methylcarbamylysulphamate was prepared by treating an alcoholic solution of the viscous methylurea salt with ammonium hydroxide (80 ml.). Pure ammonium N-methylcarbamylysulphamate was obtained, m.p. $139-140^{\circ}$ C. with decomposition. Yield, 80%. Calculated for $C_2H_9O_4N_3S$: N, 24.56%; SO_3 , 46.79%. Found: N, 24.8%; SO_3 , 46.84%.

Both salts were heated alone and with ammonium sulphamate. The results for ammonium N-methylcarbamylysulphamate are shown in Table X.

TABLE X
AMMONIUM N-METHYLCARBAMYL SULPHAMATE

Molar ratio $CH_3NHCONHSO_3NH_4$: $H_2NSO_3NH_4$	Temp., $^{\circ}$ C.	Time in minutes		Yield, %		
		Total	Above 200° C.	Methylguanidine	Guanidine	Cyanuric acid
1:0	200	29	20	Nil	Nil	92.0
1:0	230	29	20	Nil	Nil	50.0
1:0	250	30	20	Nil	Traces	40.0
1:1	200	26	20	34.0	Traces	Traces
1:2	230	26	20	85.0	Traces	Traces
1:2	250	27	20	Traces	57.0	Traces

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