

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, STANFORD UNIVERSITY]

THE CHEMICAL REACTIVITY OF THE FUSED BASES. II. THE ACTION OF FUSED POTASSIUM AMIDE UPON ALIPHATIC NITRILES¹

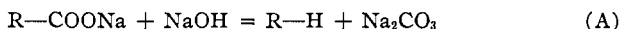
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Introduction

The preparation of methane may readily be accomplished in the laboratory by heating sodium acetate with sodium hydroxide or, better, with soda lime.² Unfortunately, the methane so prepared is never quite pure, since it is generally contaminated with hydrogen and with other gases that may arise from the decomposition of the sodium acetate alone.^{2(d-h)} Unsuccessful attempts have been made to generalize this reaction and to prepare the lower hydrocarbons of the methane series by heating the sodium salt of an acid containing one more carbon atom than the desired product with soda lime. The following equation expresses the anticipated reaction



Although some elementary organic textbooks still give this as a general method for the preparation of aliphatic hydrocarbons, it is now recognized that these reactions are rather complex and yield, besides sodium carbonate and hydrogen, quantities of hydrocarbons containing fewer carbon atoms than would be expected.³ Nevertheless, by distilling a mixture of sodium ethylate and the sodium salt of stearic, palmitic, elaidic or oleic acid in a vacuum, Mai⁴ has been able to obtain fair yields of the hydrocarbons that would be anticipated if the reaction followed the course of Equation A.

In the related field of nitrogen compounds, Miss Fulton⁵ and Mr. E. C. Cornell⁶ have found that a number of fatty acids of the ammonia system, $\text{R}-\text{C} \begin{array}{l} \text{=NH} \\ \text{---NH}_2 \end{array}$, yielded hydrocarbons when heated with potassium amide, the reactions proceeding qualitatively in accordance with the equation

¹ Presented at the Berkeley Meeting of the A. A. A. S., Pacific Division, June, 1929; from the Ph.D. thesis of R. A. Fulton.

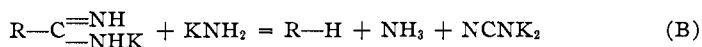
² (a) Dumas, *Ann.*, **33**, 181 (1840); (b) Berthelot, *Ann. chim.*, [3] **53**, 79 (1858); (c) Schorlemmer, *Chem. News*, **29**, 7 (1874); (d) Kolbe, "Ausf. Lehrbuch Org. Chem.," Vol. I, p. 275; (e) Moser, "Die Reindarstellung von Gasen," p. 130, Ferdinand Enke, Stuttgart; (f) Frankland and Thorne, *J. Chem. Soc.*, **33** 91 (1878); (g) Hill and Hunt, *THIS JOURNAL*, **17**, 988 (1895); (h) Freyer and Meyer, *Z. physik. Chem.*, **11**, 29 (1893).

³ Dr. H. S. Fry has obtained methane and sodium carbonate by passing the vapors of acetic acid through fused sodium hydroxide. At present Dr. Fry and his students are examining the reaction of some of the other fatty acids with the fused alkalis. Personal communication.

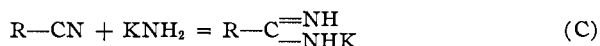
⁴ Mai, *Ber.*, **22**, 2133 (1897).

⁵ Dissertation, Stanford University, 1925.

⁶ Cornell, *THIS JOURNAL*, **50**, 3317 (1928).



The acid amidines, $\text{R}-\text{C} \begin{array}{l} \text{=NH} \\ \text{---NH}_2 \end{array}$, themselves not being readily available were prepared for the most part by the action of potassium amide on the corresponding acid anammonide (acid nitrile) as represented by the equation



The similarity between equations (A) and (B) is to be especially noted. In each case there results a hydrocarbon that contains one less carbon atom than the fatty acid entering the reaction. In the first case, potassium aquo carbonate, K_2CO_3 , is formed; in the second case, a potassium ammono carbonate, dipotassium cyanamide, NCNK_2 .

The quantitative formation of the hydrocarbon to be expected from equation (B) is scarcely to be anticipated if these reactions are strictly analogous to the decomposition of the salts of the aquo fatty acids by heated soda lime or sodium hydroxide. Therefore it becomes desirable to repeat the work of Miss Fulton and Mr. Cornell on a larger scale and under more carefully regulated conditions. To this end a number of the nitriles of the lower fatty acids were passed through molten potassium amide, in the cell described in the next section, to convert them to the potassium salts of the corresponding ammono fatty acid, in accordance with equation (C). These salts—in the presence of the heated potassium amide in the cell—were at once decomposed into di-potassium cyanamide and a mixture of hydrocarbon gases, which were collected and analyzed.

Apparatus and Manipulation

The apparatus used in the present work is shown in Fig. 1. It was fabricated entirely of nickel, since this metal appears to be unattacked by the fused amides even at temperatures well in excess of 400° .⁷ The two small needle valves were made of monel metal.

The fusion chamber F is made of a 20-cm. length of seamless nickel tube, 3.75 cm. in internal diameter and 3 mm. in thickness. A thick plug of nickel, Q, is silver soldered into the bottom of the tube in such a manner that about two-thirds of the plug projects outside. Two parallel flats are milled on this portion to permit the plug to be clamped in a vise while the hexagonal head G is being screwed into place or removed.

The nitrile is dropped from a small buret, S, into the tube P from which it is carried by a current of dry ammonia through the needle valve, A, and thence through the fused potassium amide in the bottom of the cell. The enlargement near the bottom of H is designed to prevent the fused amide from backing up into the smaller tube and solidifying. The tube T-N-H is broken at L with a compression joint, the threads on which have the same pitch as the threads on the top of F. This allows the hexagonal cap, G, to be removed at the end of a run, leaving H embedded in the solidified potassium amide. The lock-nut N allows the tip of the tube H to be adjusted at any suitable height from the bottom of the fusion chamber. Since the two valves A and D are

⁷ Fernelius and Bergstrom, *J. Phys. Chem.*, **35**, 742 (1931).

rather close together, it would be very difficult to screw both into place if it were not for the union at T.

The gases liberated in the reaction are vented through D and passed through a mercury bubbler, U, into a gas collector, V, containing dilute sulfuric acid,⁸ where the ammonia is absorbed. The unabsorbed gases are then passed through a drying tube, W, into a modified Shepherd-Porter apparatus where they are analyzed.⁹ The use of the apparatus may best be illustrated by the description of a typical run.

The thoroughly cleaned cell, assembled as in Fig. 1, is placed in a large electric crucible furnace, K, and heated to a temperature of 300° while a current of dry ammonia¹⁰ is passed through it for about half an hour. The cell is now thoroughly dry. The plug B is unscrewed and valve D closed, allowing a stream of ammonia to escape from B. Through this hole was inserted a short length of capillary sealed to the bottom of a 25-mm. test-tube. Approximately 3 g. of metallic potassium was placed in this test-tube

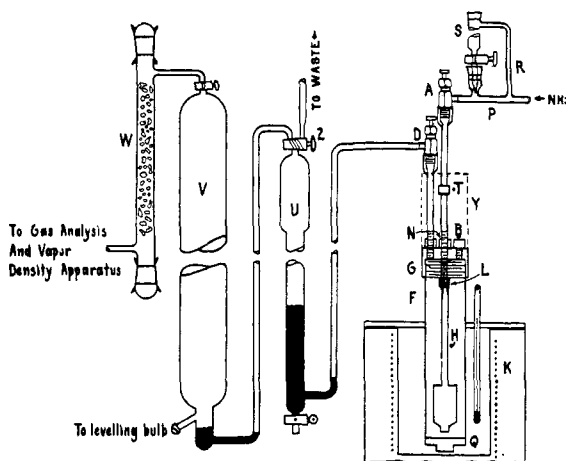


Fig. 1.

and the top closed by a stopper through which passed a tube leading to a supply of ammonia under pressure (ammonia tank).⁷ The potassium was melted by carefully applying a flame to the outside of the test-tube. The molten potassium was then forced into the cell by judicious application of ammonia pressure, the oxide remaining behind. The weight of the tube plus the potassium less the weight of the tube containing only the residual oxide equaled the weight of the potassium introduced into the cell. This generally varied between 3 and 3.5 g.

After the introduction of the potassium, B was replaced and the water jacket Y screwed into position (shown in dotted lines in Fig. 1). The jacket was kept about two-thirds full of water for the purpose of keeping the valves cool, thus facilitating their manipulation. The lock nut N was loosened and the ammonia inlet tube H adjusted so that its tip was, by calculation, about 2 mm. below the surface of the molten

⁸ Cf. Kraus and White, *THIS JOURNAL*, **45**, 768 (1923); White, *ibid.*, **45**, 779 (1923); Wooster, *ibid.*, **51**, 1859 (1929); Fernelius and Bergstrom, *J. Phys. Chem.*, **35**, 742 (1931).

⁹ Burrell, "The Recovery of Gasoline from Natural Gas," A. C. S. Monograph, p. 101. Shepherd and Porter, *Ind. Eng. Chem.*, **15**, 1143 (1923).

¹⁰ Dried over sodium according to the method of Franklin and Kraus, *Am. Chem. J.*, **23**, 285 (1900).

potassium. Then *N* was tightened. The temperature of the cell was raised to about 400° and a rapid current of ammonia passed through to convert the potassium to potassium amide (stopcock 2 was opened to the waste). This generally required about half an hour to an hour. The complete conversion was recognized by the cessation of the evolution of hydrogen. (Stopcock 2 turned to direct ammonia into the absorption tower.)

The nitrile was now introduced into the cell by means of the buret in the manner already described. Duplicate runs are comparable, since the amount of potassium used in each experiment was very closely the same and since the opening at the lower end of *I* was kept at approximately the same distance underneath the surface of the molten amide. All nitriles were passed through the cell at a rate of about 0.1 cc. per minute, that is, at such a rate that all of the nitrile reacted with the potassium amide. The weight of nitrile entering the reaction varied between one-half gram and two grams (see Table I). A more rapid rate of addition of nitrile caused the production of tar.

The gases formed in the reaction and collected in the gasholder, *V*, were passed through a barium perchlorate tube, *W*, and thence to a slightly simplified Shepherd-Porter gas analysis apparatus. The modification consisted in the use of a single tube, with indentations like a Vigreux column, for the condensation of the hydrocarbon gases by liquid air. Since the volume of gas formed in the reactions seldom exceeded one liter, a fairly complete separation of the constituents of the mixture was effected by removing the nitrogen-hydrogen, methane, ethane, propane and butane fractions with a Töpler pump, the condensation tube being held at the temperatures recommended by Shepherd and Porter. Thus, none of the hydrocarbons were re-fractionated, as in the original method to which reference was made. The efficiency of separation of the hydrocarbon gases was verified by burning them in the slow combustion pipet of the Shepherd-Porter apparatus, and by determining their vapor density. To this end the individual hydrocarbon fractions, which were collected in the graduated delivery tube of the Töpler pump, were passed through a phosphorus pentoxide drying tube and thence into an evacuated vapor density bulb. The gas so collected was weighed under a known pressure, indicated by a manometer attached to the system. The higher hydrocarbons, liquid at ordinary temperatures, were separated by repeated distillations from a small flask with a fractionating column.

The cell containing the non-volatile reaction products, together with the excess of potassium amide, was cooled in ice water and half filled with benzene. Water was then slowly introduced until the contents of the cell were completely hydrolyzed. The resulting strongly alkaline aqueous solution was separated from the benzene, diluted and almost neutralized with dilute nitric acid (cooling). Then an excess of ammonia water was added and this was followed by an aqueous solution of silver nitrate to precipitate the yellow di-silver cyanamide (silver ammono carbonate), which was filtered off, dried *in vacuo* at 60° and weighed.

It is evident that this procedure will give only an approximately accurate measure of the amount of cyanamide formed, since this is known to be slowly converted to urea in strongly alkaline solution. Buchanan and Barsky¹¹ have found that normal solutions of sodium hydroxide slowly and quantitatively convert cyanamide to urea. The rate of hydrolysis of the cyanamide is almost independent of the hydrogen-ion concentration in the more strongly alkaline solutions, the velocity constant for a first-order reaction being (0.74-0.96) 10⁻². The amount of cyanamide converted to

¹¹ Buchanan and Barsky, *THIS JOURNAL*, 52, 202 (1930).

TABLE I
RESULTS OF EXPERIMENTS

Nitrile	A RCN added, g.	B ^a Gas formed, cc.	C Mol. wt. of hydrocarbons			D Calcd. mol. wt.	E Di-silver cyanamide g.	F Mo'les of di-silver cyanamide, per mole of RCN	G Temp., °C.
CH ₃ CN ^b	2.21	1197.3	15.92			16.0	13.683	1.0 ± 300	
CH ₃ CN	1.82	973.2	16.11			16.0	11.162	1.0 ± 360	
CH ₃ CN	1.24	618.3	15.89			16.0	7.458	1.0 ± 400	
CH ₃ CH ₂ CN	1.68	897.4	15.95	27.72		16.0 30.0	9.876	1.24 300	
CH ₃ CH ₂ CN	1.13	753.2	15.92	29.87		16.0 30.0	7.217	1.35 360	
CH ₃ CH ₂ CN	1.28	826.9	15.97	29.92		16.0 30.0	9.089	1.49 400	
CH ₃ CH ₂ CH ₂ CN	1.35	613.4	15.8	29.3	43.9	16.0 30.0 44.1	6.132	1.207 300	
CH ₃ CH ₂ CH ₂ CN	1.52	763.8	15.9	29.8	43.7	16.0 30.0 44.1	8.197	1.43 360	
CH ₃ CH ₂ CH ₂ CN	1.19	686.2	15.9	29.9	43.8	16.0 30.0 44.1	7.973	1.78 400	
CH ₃ CH ₂ CH ₂ CH ₂ CN	0.92	403.2	15.8	29.9	43.9 57.7	16.0 30.0 44.1 58.1	4.587	1.61 300	
CH ₃ CH ₂ CH ₂ CH ₂ CN	0.74	337.2	15.9	30.1	43.9 57.8	16.0 30.0 44.1 58.1	3.968	1.69 360	
CH ₃ CH ₂ CH ₂ CH ₂ CN	0.87	447.4	15.8	30.0	44.2 58.9	16.0 30.0 44.1 58.1	5.149	1.88 400	
(CH ₃) ₂ CHCH ₂ CH ₂ CN	0.81	282.2	16.1	30.2	58.1 71.9	16.0 30.0 58.1 72.1	1.985	0.94 300	
(CH ₃) ₂ CHCH ₂ CH ₂ CN	0.55	233.7	16.2	30.1	58.2 71.8	16.0 30.0 58.1 72.1	1.523	1.05 360	
(CH ₃) ₂ CHCH ₂ CH ₂ CN	0.68	321.0	16.1	30.2	58.3 71.9	16.0 30.0 58.1 72.1	2.140	1.19 400	

^a Under standard conditions. ^b All nitriles were dried over phosphorus pentoxide, separated from the latter and redistilled.

urea during the hydrolysis of the potassium amide fusions here discussed should not exceed a very few per cent. The analytical results for cyanamide are thus only approximately correct, especially since the di-silver cyanamide precipitates are often impure.

Results of the Experiments

The experiments described in this paper were all performed in duplicate, the conditions of the two sets of runs being as nearly identical as possible. The analyses of the gases formed in the two runs checked to within a few tenths of one per cent. in nearly all cases. Undoubtedly alteration in the speed of addition of the nitrile and in the height of fused potassium amide through which the nitrile was passed would alter the relative proportions of the hydrocarbons that were formed. The average values are given.

Table I shows the weight of the nitrile entering the reaction at the three temperatures of the experiments (300, 360 and 400°) (column A); the total volume of gas formed (column B); the molecular weight of the hydrocarbon fractions as determined by the vapor density method (column C); the calculated molecular weights of these hydrocarbons (column D); the weight of di-silver cyanamide obtained from the hydrolyzed solid reaction product (column E), and the number of moles of di-silver cyanamide obtained per mole of the reacting nitrile (column F).

Tables II, III and IV summarize the results of the analyses of the gases whose volumes are given in column B of Table I.

TABLE II
THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE
(Temp., 300°)¹²

	Hydrogen	Methane	Ethane	Propane	Butane	Iso- butane	Iso- pentane
CH ₃ CN	1.8	98.2					
CH ₃ CH ₂ CN	18.6	16.4	65.1				
CH ₃ CH ₂ CH ₂ CN	16.1	14.5	11.6	57.8			
CH ₃ CH ₂ CH ₂ CH ₂ CN	52.3	1.9	2.8	10.6	32.4		
(CH ₃) ₂ CHCH ₂ CH ₂ CN	59.3	Trace	2.5			9.5	28.7

Discussion

It is evident that potassium amide and acetonitrile react at all three temperatures to form methane and dipotassium cyanamide in almost theoretical yields, in accordance with the type equation B. Propionitrile and solid potassium amide react at 300° to form a gas which is 65% ethane,

¹² The nitrogen-hydrogen-methane fraction, pumped from the solidified hydrocarbon gases at liquid air temperatures, was analyzed by combustion in a slow combustion pipet, the amount of methane being determined from the carbon dioxide formed in the reaction. The remainder of the combustible gas, as calculated from the contraction in volume on burning with air was hydrogen. However, since nitrogen was not obtained in significant amounts in the preliminary runs, the hydrogen in the above tables was determined by difference, the volume of methane being known.

TABLE III
THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE
(Temp., 360°)

	Hydrogen	Methane	Ethane	Propane	Butane	Iso-butane	Iso-pentane
CH ₃ CN	2.2	97.8					
CH ₃ CH ₂ CN	26.7	22.8	50.6				
CH ₃ CH ₂ CH ₂ CN	22.8	21.1	12.3	43.8			
CH ₃ CH ₂ CH ₂ CH ₂ CN	57.2	2.2	3.5	11.4	25.6		
(CH ₃) ₂ CH ₂ CH ₂ CH ₂ CN	63.8	0.03	3.2			10.7	21.3

TABLE IV
THE DECOMPOSITION OF NITRILES BY POTASSIUM AMIDE
(Temp., 400°)

	Hydrogen	Methane	Ethane	Propane	Butane	Iso-butane	Iso-pentane
CH ₃ CN	2.5	97.5					
CH ₃ CH ₂ CN	39.7	32.4	27.9				
CH ₃ CH ₂ CH ₂ CN	42.5	31.6	10.5	15.4			
CH ₃ CH ₂ CH ₂ CH ₂ CN	63.9	2.2	3.5	11.4	25.6		
(CH ₃) ₂ CH ₂ CH ₂ CH ₂ CN	71.5	4.2	5.6			13.8	4.9

16.4% methane and 18.6% hydrogen. All of the higher nitriles behave similarly, that is, the expected hydrocarbon is formed, together with varying amounts of all of the hydrocarbons down to and including methane. Hydrogen is always formed at the same time.

The yields of the lower hydrocarbons and of hydrogen increase with increasing temperature of fusion (Tables III and IV), while the yield of the expected hydrocarbon (equation A) decreases. This points most obviously to a catalytic decomposition or cracking of the expected hydrocarbon which increases with increasing temperature. The nickel of the cell at the temperatures of the reactions was found to have little effect on vapors of the hydrocarbons below pentane, when these were passed through the empty cell. The potassium amide itself must therefore have caused the decomposition or cracking of the anticipated hydrocarbons. This was indeed found to be the case, since the hydrocarbons from *n*-heptane down to ethane were partially cracked when passed through molten potassium amide under the conditions of the present experiments. This work will be discussed in detail in a forthcoming paper.

In an entirely analogous manner it was found that *n*-pentane was cracked readily by soda lime at a temperature of 400°, yielding hydrogen and a mixture of the lower hydrocarbons with a large preponderance of methane. This will perhaps account for the impracticability of preparing ethane and its higher homologs in accordance with the generalized reaction of equation A.

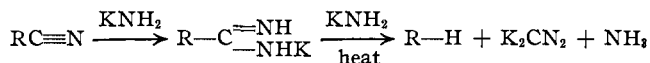
The decomposition of some of the higher nitriles by fused potassium amide (Table I) has given more than one mole of cyanamide per mole of

reacting nitrile. It is known that carbon may be converted by the fused amides to cyanamide.¹³

Summary

1. A nickel apparatus has been devised for carrying out reactions in pure fused sodium or potassium amides.

2. The ammono fatty acid anammonides—that is, the nitriles of the fatty acids—react with fused potassium amide in accordance with the type equation



In other words, the salts of the fatty acids of the ammonia system are decomposed by heating with a base of the same system into a hydrocarbon and a sodium ammono carbonate (di-sodium cyanamide). The hydrocarbon R—H is cracked by the molten amide to simpler hydrocarbons and hydrogen, the degree of decomposition increasing with increase in the temperature of the fusion.

3. The failure to obtain the expected hydrocarbon in the reaction $\text{R}-\text{COONa} + \text{NaOH}$ (heated) = $\text{Na}_2\text{CO}_3 + \text{R}-\text{H}$ appears to be due in part at least to the cracking of the expected product R—H to lower hydrocarbons and hydrogen under the catalytic influence of soda lime or sodium hydroxide.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE CONSTITUTION OF MELEZITOSE AND TURANOSE

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Investigations¹ have shown that when the natural non-reducing trisaccharide melezitose is gently hydrolyzed by weak acid solutions, there results as one of the products the reducing disaccharide, turanose. This sugar is the first known true isomer of sucrose and was first obtained in a pure crystalline condition by C. S. Hudson and the present author.² The failure in the past to secure a crystalline turanose has compelled investigators to use melezitose as the starting material in their efforts to solve the problem of the constitution of these two sugars.

¹³ English Patents 12,219; 21,732 (1894). German Patents 117,623; 124,977; 126,241 (1900); 148,045 (1901). Cf. *Chem. Zentr.*, [I] 75, 411 (1904).

¹ Alekhine, *Ann. phys. chim.*, 18, 532 (1889); G. Tanret, *Bull. soc. chim.*, [3] 35, 816 (1906); R. Kuhn and G. E. von Grundherr, *Ber.*, 59, 1655 (1926).

² C. S. Hudson and E. Pacsu, *Science*, 69, 278 (1929); *THIS JOURNAL*, 52, 2519 (1930).