Acetylene-Ammonia Condensation

CATALYZED BY THE PRESENCE OF MOLTEN SALTS

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The condensation of acetylene with ammonia in the presence of molten zinc chloride was investigated with the hope of synthesizing pyridine compounds. However, acetonitrile of 75 to 85% purity was obtained as the main product in yields up to about 60%. The nature of the condensation products was unaffected by reaction conditions. The reaction was studied by passing the reactant gases and molten salt catalysts in direct contact countercurrent to each other in a wetted-wall column as a means for controlling the highly exothermic reaction. Several molten salt systems were tested, but only those containing zinc chloride were active catalysts. At a given temperature level within the range of 440° to 550° C. an optimum concentration of zinc chloride was found for maximum yield of liquid products. Similarly at a given concentration of zinc chloride an optimum temperature was found for maximum yield. At 510° C. this concentration was about 40 mole % zinc chloride. A threshold temperature of 430° C. was found below which no condensation took place due to inhibition of the catalyst by formation of a stable ammonia–zinc chloride complex. The diluent alkali chlorides used with zinc chloride had a marked effect on catalyst activity. The mole ratio of acetylene to ammonia should be low, about 1 to 1, for best results.

THE work described in this paper was carried out in the hope of synthesizing pyridine, of which there was a critical shortage in the war effort.

Acetylene and ammonia, both of which could be made available as raw materials, will react to form pyridine along with other products. The yields of pyridine from this condensation have not been encouraging largely because of uncontrolled and undesirable side reactions. The recent work of Johnson and Swann (*8*) involving the use of the molten chlorides of zinc, potassium, and sodium in the condensation of acetylene with itself to produce aromatic hydrocarbons in good yields suggested a means by which the condensation of acetylene with ammonia might be carried out satisfactorily. The literature on the subject of molten salts as catalysts has been reviewed by Johnson and Swann (*8*).

Numerous patents and a few published articles have been found on the condensation of acetylene with ammonia. The conditions under which the reaction has been carried out are many and varied. Generally, solid catalysts have been used, such as cadmium oxide on acidic white clay (*19*), zinc chloride on pumice (*13, 16*), finely dispersed lead, cadmium, bismuth, or gold on silica gel (*3, 20*), the oxides of iron, zinc, or aluminum (*17*), zinc trichloroacetate on pumice (*14*), bauxite (*29*), zinc sulfate (*6*), zirconium and thorium oxides (*25*), ferric chloride on pumice (*15*), and zinc oxide, chromium oxide, and magnesium chloride (*21*). The temperature of the reaction has been varied from 250° C. (*9–11*) to about 600° C. (*12*) and mole ratio of reactants varied considerably. Diluents such as hydrogen, methane, and steam are reported. It appears that in all investigations a wide variety of products was formed. Usually di- and triethylamine, acetonitrile, pyridine, picolines, higher nitrogen heterocycles, and higher hydrocarbons are found in varying amounts in the products of the reaction.

The patent literature may be classified into two groups according to the major product claimed for the condensation. One group (*3, 5, 13, 14, 16, 17, 20, 22, 26*) claims the formation of pyridine with lesser amounts of acetonitrile and the other (*2, 4, 6, 15, 21, 23–25, 29*) acetonitrile with lesser amounts of pyridine. It was hoped in the present work that with good temperature control possible by the use of molten salt catalysts higher yields of pyridine compounds would be obtained.

REACTION VARIABLES

MOLTEN SALT CATALYSTS. Johnson and Swann (*8*) discuss the limitations of molten salt systems which reduce the number available for investigation to relatively few. In addition to the limitations of melting point, stability, and toxicity, the formation of ammines between ammonia and components of the molten salt bath was found to be undesirable, but this was a limiting factor only in the case of zinc chloride. Most of the salts form ammines but in all of the other cases, the ammines decompose at temperatures below the melting point of the system. With these limitations five systems were found which could be tested for catalytic activity:

1. Zinc chloride–potassium chloride–sodium chloride
2. Cadmium chloride–potassium chloride–sodium chloride
3. Lead chloride–potassium chloride–sodium chloride
4. Ferric chloride–potassium chloride–sodium chloride
5. Stannous chloride–potassium chloride

TEMPERATURE RANGE. Some calculations of the free energy of formation of pyridine by Equation 1 were made to determine if there was a particular temperature range thermodynamically favorable for the reaction.

$$3C_2H_2 + NH_3 \longrightarrow C_5H_5N + CH_4 \qquad (1)$$

At all temperatures in the operating range of the apparatus the formation of pyridine is favorable. Free energy values of −120,000 calories per gram mole were found at 100° C. and −90,000 calories at 570° C. Acetonitrile formation by Equation 2 is also favorable.

$$C_2H_2 + NH_3 \longrightarrow CH_3CN + H_2 \qquad (2)$$

In this case the values of free energy of formation over the same temperature range are −12,000 to −8,000 calories per gram mole. In view of Johnson and Swann's results (*8*) where condensation of acetylene with itself was shown to be appreciable at temperature of about 550° C., this temperature was chosen as

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the upper limit of the range to be investigated. The lower limit was fixed for each molten salt system by the fusion point of the system. A safe margin of about 75° C. above this fusion point was necessary to avoid freezing of the salts in the apparatus.

MOLE RATIO OF ACETYLENE TO AMMONIA. Most of the work was carried out using a mole ratio of acetylene to ammonia of 3 to 1 which represents stoichiometric amounts of the reactants for the formation of pyridine by Equation 1. The mole ratio was varied within the limitations of the apparatus in one series of runs.

CONTACT TIME. A contact time of approximately 5 seconds was shown to be satisfactory in preliminary runs. This value was used through the remainder of the work.

CHEMICALS USED

ACETYLENE. Welding acetylene was used in all runs. The gas was purified by passing it through a train consisting of three wash bottles, sodium hypochlorite, 5.25%; sodium hydroxide, 50%, and sulfuric acid, 75%, followed by a calcium chloride drying tower.

AMMONIA. Liquid ammonia in a 60-pound tank was used. The ammonia gas was passed through a strontium oxide drying tower as a precaution against moisture.

MOLTEN SALTS. The various molten salt systems tested were made up of C.P. grade chemicals. Anhydrous salts were used where possible. In the cases where anhydrous salts were not available dehydration was accomplished merely by heating to relatively high temperatures for a long enough period to allow the water vapors to escape. The melts were prepared by mixing the chlorides in the proper proportions and heating to a temperature sufficient to ensure homogeneity of the melt. The molten salts were then poured into ceramic crucibles and allowed to harden. The salts were broken up and stored in stoppered bottles until used.

APPARATUS

The experimental apparatus was similar to that described by Johnson and Swann (*8*). Changes were necessary in the reactant gas flow rate control and in the means for recovering liquid products because of differences in the reaction.

The rate of flow of acetylene was controlled by a needle valve upstream from an orifice meter. An inclined, water-filled manometer was used to measure the differential pressure across the orifice. Several orifices were constructed and calibrated to cover the range of the flow rates used. The ammonia flow was handled in a similar fashion. In some of the runs where hydrogen was used as a diluent, a third orifice meter was installed.

The condensing system for the recovery of the liquid product consisted of three condensers in series operated at 25° C. (air cooled), 12° C. (water cooled with iced receiver), and −10° C. (salt water–ice cooled). Generally the major portion of the liquid product was collected in the ice-cooled receiver to the water condenser. The light ends were removed in a long condenser filled with a saturated salt water–ice brine at a temperature of −8° to −10° C. A dry ice and alcohol trap could not be used because at the temperature of operation of such a trap, ammonia is condensed out of the off-gas stream interfering with the subsequent analysis for unreacted ammonia.

PROCEDURE

The technique for carrying out experiments employing molten salts in glass columns has been described by Johnson and Swann (*8*). Except that the condensation of acetylene with ammonia was found to take place immediately without the induction period observed in the earlier work and without formation of graphitic carbon as a precursor to reaction, the techniques were essentially alike.

The apparatus must be purged with methane or nitrogen before and after each run to avoid ignition of acetylene which occurs spontaneously in the presence of air at the temperatures of operation used in this work. Precautions should naturally be taken in handling the molten salt catalysts to avoid inhaling the vapors.

ANALYTICAL. The analysis of the noncondensable gases for unreacted ammonia and acetylene could not be carried out in an Orsat apparatus because of interference by one or the other of these materials. It was suggested (*28*) that the ammonia could be absorbed rapidly and quantitatively by means of magnesium perchlorate. When a test of the magnesium perchlorate showed no absorption of acetylene, it was decided to employ this reagent.

The method used for obtaining the off-gas composition consisted in passing the gases over a weighed amount of magnesium perchlorate for 5 to 10 minutes. During this time a sample of the ammonia-free gas was collected. The acetylene present in the sample was determined by absorption in a solution made up of 20 grams of mercuric cyanide dissolved in 100 ml. of 2 *N* sodium hydroxide and the inerts were measured by difference.

The liquid condensation product obtained in each run was distilled in a small, vacuum-jacketed, indented column. The efficiency of this column was low, but sufficient for the separation required. The density of the liquid product was determined before distillation by weighing a 5-ml. pipeted sample to 0.0005 gram.

Acetonitrile, which was the major product in all cases, was identified by means of its refractive index, boiling point, density, and its ethyl iminomercaptoacetic acid hydrochloride (*27*).

DISCUSSION OF RESULTS

PRELIMINARY RUNS. A series of 16 preliminary runs was made during which the catalytic activity of various molten salt systems was tested. Several runs were first made in which the catalyst consisted of a ternary salt system with zinc chloride as the active component. The system contained 54 mole % zinc chloride, 25 mole % potassium chloride, and 21 mole % sodium chloride. This mixture has a melting point of 206° C. (*18*) and is a colorless mobile liquid in the molten state. It was used because its melting point allowed operation at a temperature of 300° to 400° C. which was thought desirable for a smooth reaction.

Several runs were made at 375° C., some in the column previously described (*8*), and five using a bubbler in which the reactant gases were allowed to pass through a test tube filled with the melt. In none of these runs was any liquid obtained. However, with the bubbler type of reactor it was noted that either the reactants or products were apparently reacting with the fused salts, as evidenced by the formation of a stable froth on the surface of the salts. The salts were more viscous and did not crystallize readily after cooling. It was thought that any complex formation with the ammonia or acetylene and zinc chloride would result in an unstable compound at the temperature of operation, but the appearance of the bubbler indicated that this was not the case. A portion of the salts from one of the runs was crushed and added to a strong caustic solution. In the presence of the caustic an odor resembling that of ammonia was given off, indicating that ammonia had formed a complex with the zinc chloride which was not decomposed at 375° C. Upon further investigation of the literature it was found (*1*) that ammonia and zinc chloride form an equimolar complex which is stable up to a temperature of 430° C.

Then three runs were made at temperatures of 325°, 375°, and 440° C. to test the possibility of catalytic inhibition in the presence of the zinc chloride–ammonia complex. The apparatus used in these and all subsequent runs was that mentioned earlier (*8*). A contact time of 5 seconds and mole ratio of acetylene to ammonia of 3 to 1 were the conditions. In the run at 325° C. very little reaction of any kind was noted. The run at 375° C. was similar to earlier runs at this temperature and no liquid condensation product was found. The third run at 440° C. was successful. Over a period of 8.5 hours, 24 ml. of liquid product were obtained. Condensation was regular throughout the run. The column was black with carbon, but the salts were reasonably clean.

It was concluded that the zinc chloride–potassium chloride–sodium chloride system was an active catalyst for the condensation at temperatures of operation higher than 430° C. Strong evidence was found for the belief that complex formation between reactants and the molten salt system used as catalyst in-

Table I. Summary of Data for Runs 17 through 31

Run No.	Catalyst Composition, Mole %				Temp., ° C.	Mole Ratio $C_2H_2:NH_3$	C_2H_2 In, G.	NH_3 In, G.	C_2H_2 Out, G.	NH_3 Out, G.	Inert Out, G.	Liquid Product, G.	Conversion[a], %	Yield[b], %	Inert[c], %
	$ZnCl_2$	KCl	NaCl	LiCl											
17	54	25	21		440	3.0	153.7	34.5	85.9	9.3	11.6	40.4	21.5	43.5	15.8
18	54	25	21	..	470	3.0	82.6	22.4	37.6	3.3	7.4	28.0	26.7	43.7	21.9
19	28.5	59	12.5	..	470	3.0	65.9	14.8	54.3	15.2	0.8	0	0	0	1.6
20[d]	28.5	59	12.5	..	470	3.0	53.5	11.7	43.4	12.4	1.2	1.5	2.3	16.0[e]	3.0
21	40	..	60	..	470	3.0	218.0	47.3	148.0	28.8	14.3	36.1	13.6	40.8	10.8
22	40	..	60	..	550	3.0	88.4	19.4	40.6	8.4	9.2	27.6	25.6	47.0	21.8
23	40	..	60	..	510	3.0	192.2	45.4	127.4	20.5	16.9	43.8	18.5	48.9	14.7
24	40	..	..	60	510	3.0	80.3	17.5	31.9	4.5	10.8	36.3	37.1	59.1	31.0
25	40	60	..	..	510	3.0	144.5	32.0	114.4	20.7	7.5	14.8	8.4	35.8	7.7
26	..	42	..	58	510	3.0	81.9	17.9	75.0	17.6	0	0	0	0	0
27	40	..	60	..	510	1.0	133.8	83.9	79.9	64.2	15.7	41.4	19.0	56.2	12.5
28	40	..	60	..	510	5.0	205.0	28.4	143.8	24.6	7.3	29.9	12.8	46.0	7.7
29	40	..	60	..	510	0.33	24.8	45.8	..	..	..	9.4	19.3[f]	...	..
30	40	..	60	..	510	1:2:5.7[g]	13.4	17.5	10.4	17.8	6.0	0.5	1.3	16.7	67.5
31	40	..	60	..	510	1:1:3.5[h]	32.6	22.4	20.6	34.6	7.8	3.6	9.2	36.5[e]	63.4

[a] Wt. of liquid ÷ total wt. of reactants.
[b] Wt. of liquid ÷ total wt. of reactants disappearing.
[c] Vol. % in off gases.
[d] Contact time 8 seconds, in all other runs 5 seconds.
[e] Assumes excess ammonia out is product.
[f] Conversion calculated assuming liquid is acetonitrile, gas analysis was not possible for this run.
[g] Third component is hydrogen, 6.0 g. were charged, inert out is hydrogen.
[h] Third component is hydrogen, 8.0 g. were charged, inert out is hydrogen.

hibits catalytic activity. No further work was done on this system in the preliminary studies.

A ternary eutectic mixture of 33 mole % cadmium chloride, 43 mole % potassium chloride, and 24 mole % sodium chloride (*7*) was evaluated next. This salt system is colorless, of low viscosity, and has a density greater than Pyrex. A run was made at 440° C., 5 seconds contact time, and mole ratio of acetylene to ammonia of 3 to 1. At the conclusion of 3 hours' operation with this catalyst no liquid product was obtained. The salts were still colorless, apparently unchanged. A little carbon was found deposited in the column, indicating some decomposition of acetylene which was to be expected at this temperature. It was concluded that the system was inactive under the conditions used. No further work was carried out with cadmium chloride.

A eutectic mixture containing 36.8 mole % ferric chloride, 36.8 mole % potassium chloride, and 26.4 mole % sodium chloride was tried next. The melt was prepared in the usual manner. After the mixture was first heated to a temperature of about 200° C. to form a homogeneous solution, the material solidified slowly, first passing through a mushy, amorphous stage. The molten salts so prepared are red-brown in color and do not have a sharply defined melting point. The melting point was found to be 150° to 160° C. An attempt was made to carry out the run at 275° C. It was not possible to circulate the salts by means of the glass pumping mechanism used because of the formation of insoluble material which jammed the check valves. It was found that after a test tube of the salts had been heated for a short time, a layer of insoluble material (probably ferric oxide) was deposited on the bottom. This system was therefore discarded as too unstable for use in the present apparatus.

A eutectic mixture containing 48 mole % lead chloride, 38 mole % potassium chloride, and 16 mole % sodium chloride was prepared for evaluation. This mixture was a pale yellow, highly mobile liquid with a density greater than that of Pyrex, and with a melting point of 387° C. (*7*). The run was made at a temperature of 475° C. After 3 hours of operation no liquid product was obtained and the salts were clean. A small amount of carbon was deposited in the column. It was concluded that lead chloride was not a catalyst under these conditions. This was not in agreement with some limited data obtained by Johnson and Swann (*8*) for the condensation of acetylene alone where they found that a lead chloride catalyst was active. No further work was done with lead chloride in the present investigation.

Stannous chloride was the catalyst for the next run. It was prepared by heating a mixture of stannous chloride dihydrate and potassium chloride. At 140° C. the solution appeared to boil and water vapor was given off. As the water came out of the mixture the melting point rose to about 240° C. The molten salts resulting were a very pale green and had a low viscosity. The run was carried out at a temperature of 350° C. and was discontinued after a period of 30 minutes because the column cracked. Apparently some liquid was formed although not enough to measure in the short period of operation.

The run was repeated at a temperature of 310° C. but a crack in the pumping system forced a temporary shutdown shortly after arriving at the operating temperature. The salts were kept molten at 300° C. while repairs to the apparatus were made. When the run was resumed, no product was obtained in 3 hours of operation. Since the salts used in this run had twice been allowed to solidify in air, it was thought that the stannous chloride was possibly converted at least partially into basic stannous chloride. Therefore a third run was made in order to see if the reaction of stannous chloride with oxygen was inhibiting the catalytic activity of the salts. All feasible precautions were taken in preparing the salts to exclude air. The run was started without the difficulty encountered in the previous runs with this system. Apparently during the first 15 minutes of the run some condensation took place, but only enough so that the product appeared as small drops on the walls of the condenser. After this period no more reaction was observed. Since the salts in the reservoir were unavoidably exposed to air, it was thought that the stannous chloride was rapidly converted into some other compound which was not a catalyst for the condensation or which inhibited any unconverted stannous chloride. In confirmation of this observation was the occurrence of a layer of solid material which separated from the molten salts and collected in the bottom of the reservoir. Because some product was formed initially, stannous chloride may be active; but it was not suitable for use in the present apparatus.

These sixteen runs constituted the preliminary study of the reaction. Of the salts tested only the system containing zinc chloride proved to be suitable as a catalyst. Cadmium chloride, lead chloride, ferric chloride, and stannous chloride mixed with potassium, and sodium chlorides were inactive or unsuited to the apparatus.

Zinc Chloride Systems. The study of zinc chloride as a catalyst for the condensation of acetylene with ammonia involved several series of runs. The influence of zinc chloride concentration in a mixture containing potassium and sodium chlorides was investigated first. Runs 17 to 21, inclusive, were made with this object in view. Runs 21, 22, and 23 illustrate the effect of temperature with the binary salt system zinc chloride–sodium chloride. Runs 22 to 26, inclusive, were made to show the effect of the diluent alkali chloride in binary mixture with zinc chloride. The mole ratio of acetylene to ammonia was varied within the limits of the apparatus in runs 27, 22, 28, and 29 with zinc chloride–sodium chloride as catalyst. The reactant gases were diluted with hydrogen in runs 30 and 31. Finally two runs were made with acetonitrile and acetylene in

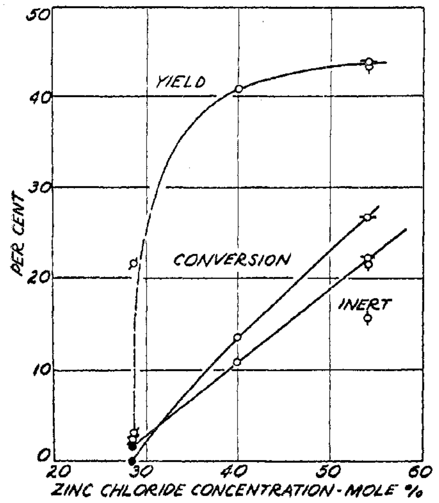

Figure 1. Influence of Zinc Chloride Concentration

470° C., 5 seconds' contact time, and 3:1 mole ratio of acetylene to ammonia

● Run 19, 28.5% $ZnCl_2$
○ Run 20, 28.5% $ZnCl_2$ (8 seconds' contact)
○ Run 21, 40.0% $ZnCl_2$
-○- Run 18, 54.0% $ZnCl_2$
○ Run 17, 54.0% $ZnCl_2$ (440° C.)

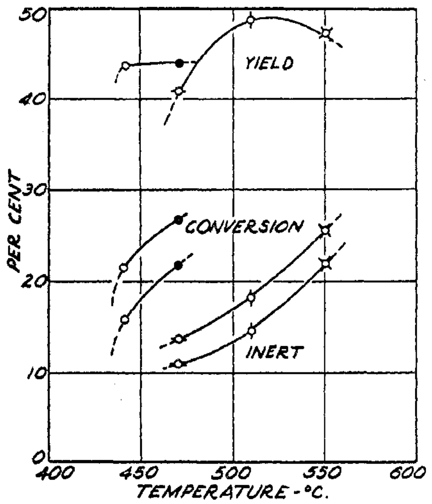

Figure 2. Influence of Temperature

$ZnCl_2$ concentrations of 54 and 40 mole % with 5 seconds' contact time and 3:1 mole ratio of acetylene to ammonia

○ Run 17, 54% $ZnCl_2$ (440° C.)
● Run 18, 54% $ZnCl_2$ (470° C.)
-○- Run 21, 40% $ZnCl_2$ (470° C.)
○ Run 23, 40% $ZnCl_2$ (510° C.)
○ Run 22, 40% $ZnCl_2$ (550° C.)

the presence of zinc chloride–potassium chloride–sodium chloride. The data for runs 17 through 31 are summarized in Table I.

INFLUENCE OF ZINC CHLORIDE CONCENTRATION. Runs 17 and 18 made with the ternary eutectic containing 54 mole % zinc chloride at 440° and 470° C., respectively, indicated that this system was active. In both runs the column was very black and the salts covered with carbon. During the runs carbon smoke was given off from the surface of the salts in the reservoir so that losses of 21% were noted. It was thought that this activity is due to a loose coordination complex formed between the zinc ions and ammonia. If this were the case, a reduction in the zinc chloride concentration should bring about a smoother reaction with less carbonization. Consequently runs 19 and 20 were carried out with a ternary salt system containing 28.5 mole % zinc chloride (*18*). In run 19 at 470° C. no liquid product was obtained after 3 hours of operation. The contact time was increased from 5 to 8 seconds in run 20, all other conditions remaining constant; and in this case, about 2 ml. of liquid were collected in 4 hours. The material balance showed a gain for ammonia because any basic product formed and not completely condensed owing to its low partial pressure in the off-gases was analyzed as ammonia since such material would be absorbed by the magnesium perchlorate. This run, the only one in which a 5-second contact time was not used, illustrates that some reaction could be made to occur with a catalyst containing a relatively low concentration of zinc chloride.

A comparison of the results of runs 18 and 20 indicated that a zinc chloride concentration intermediate between 54 and 28.5 mole % would give the best results at 470° C. In order to obtain a system containing zinc chloride in such a concentration with a melting point in the proper range, it was necessary to resort to a binary mixture of zinc and sodium chlorides. The system chosen (*30*) has a melting point of 370° C. (*31*) and contains 40 mole % zinc chloride. Run 21 was carried out using this system at a temperature of 470° C. The salts from the run were moderately dark, giving evidence of some carbon formation but the heavy fumes noted in runs 17 and 18 were absent.

The influence of zinc chloride concentration in the molten salts used as catalysts is illustrated in Figure 1. In comparing runs 18, 19, and 21 it must be kept in mind that the diluent alkali chloride composition and concentration were also varied. As was shown in a later series of runs, the diluent used has a marked effect on the activity of the zinc chloride. As to the curves in Figure 1, the conversion of liquid is seen to be directly proportional to the zinc chloride concentration at 470° C. The yield falls off rapidly as the concentration is reduced below 40 mole %. Probably the yield curve goes through a maximum, since decomposition occurring at high activity with concentrations over 54 mole % would result in loss of product.

INFLUENCE OF TEMPERATURE OF REACTION. The effect of temperature on the condensation in the presence of the binary system zinc chloride–sodium chloride was investigated in runs 21, 22, and 23. The appearance of the reaction chamber after run 22 at 550° C. suggested that more material of higher molecular weight was produced at this temperature than at the lower temperature of run 21. The entrance tube to the condensing system was coated with a tarry material not previously noted. Run 23 at 510° C. gave the maximum yield and the smoothest reaction. The same batch of salts was used in all three runs. No loss in activity was observed through a total of 25 hours on stream with repeated heating and cooling of the salts. Throughout the investigation evidence was obtained which showed the salts to have no detectable decrease in catalyst life. Johnson and Swann also found that zinc chloride was an extremely rugged catalyst and that the salts could be used over and over again.

Figure 2 illustrates the effect of temperature on the condensation at two concentrations of zinc chloride. A distinct maximum occurs at 510° C. in the presence of 40 mole % zinc chloride. Conversion is seen to be approximately linear with temperature. Probably there exists at any temperature level within the range of catalyst activity an optimum concentration of zinc chloride for optimum yields; and conversely for any concentration, an optimum temperature of reaction.

INFLUENCE OF DILUENT ALKALI CHLORIDE. A series of runs was made to evaluate the activity of the alkali chloride diluent admixed with zinc chloride in order to arrive at a basis for comparison of runs 17, 18, and 19 where ternary systems were used with runs 21, 22, and 23 where binary systems were catalysts. Run 24 was carried out with a catalyst consisting of 40 mole % zinc chloride and 60 mole % lithium chloride. This molten salt system is similar in physical properties to the zinc chloride–sodium chloride bath and melts at approximately 350° C. The temperature used was 510° C. which was the same as for run 23. After 4 hours of operation the run was discontinued because of excessive fuming of the salts in the reservoir and because of a tendency toward plugging of the off-gas line. The salts were black with carbon and in general the results showed high catalyst activity.

Run 25 was then carried out using 40 mole % zinc chloride and 60 mole % potassium chloride to complete the survey of diluent alkali chlorides. The activity of this bath was very low compared to that used in run 24. The apparatus showed the usual effect of lessened catalyst activity with much less carbon deposited. In order to show whether the alkali chlorides were acting as catalysts or merely as diluents to the zinc chlorides, run 26 was made with a molten salt mixture containing 58 mole % lithium chloride and 42 mole % potassium chloride. After 4 hours of operation no condensation was observed. The material balance on this run showing a loss of 7% is probably typical of the accuracy obtainable with the apparatus.

The data are plotted in Figure 3. The yield and conversions are seen to be approximately proportional to the molecular weight of the alkali chloride used as diluent. When no zinc chloride was present in run 26, no reaction occurred. Therefore the alkali chlorides are not in themselves catalyst for the condensation. Because they do promote the reaction in proportion to their molecular weights credence is given the theory that shielding of the zinc ion is responsible for the trend in activity noted. The smaller lithium chloride molecules cannot isolate the zinc chloride as effectively as sodium chloride and therefore the activity of the zinc chloride is increased. The same effect could be produced with sodium chloride by increasing the concentration of zinc chloride.

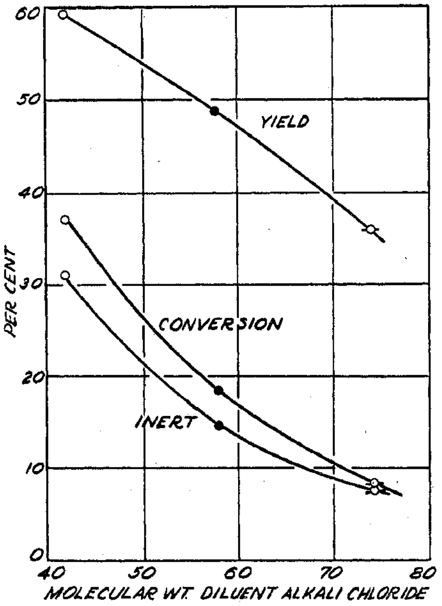

Figure 3. Influence of Diluent Alkali Chloride

40 mole % $ZnCl_2$ at 510° C., 5 seconds' contact time, and 3:1 mole ratio of acetylene to ammonia

○ Run 24, 60% LiCl
● Run 23, 60% NaCl
-○- Run 25, 60% KCl

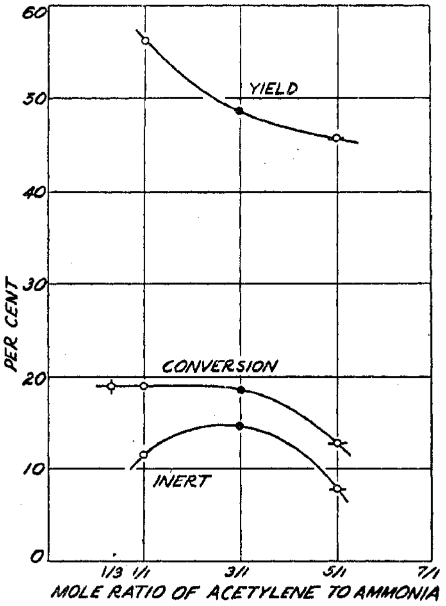

Figure 4. Influence of Mole Ratio of Acetylene to Ammonia

40% $ZnCl_2$–60% NaCl at 510° C. and 5 seconds' contact time

ϕ Run 29, 1:3
○ Run 27, 1:1
● Run 23, 3:1
-○- Run 28, 5:1

INFLUENCE OF MOLE RATIO OF ACETYLENE TO AMMONIA. Run 24 with zinc chloride–lithium chloride gave the largest yield at 510° C. of any of the binary mixtures tested. However, more carbon formation and undesirable decomposition also occurred with this catalyst. On the other hand, zinc chloride–sodium chloride gave a smoother reaction with good yield of condensation product and for this reason was used as the catalyst in evaluating the effect of mole ratio of acetylene to ammonia. In run 27 the mole ratio was reduced to 1 to 1 compared to 3 to 1 for run 21. In this run carbon formation was light and the salts were clean. Apparently the reaction proceeded smoothly with little tar formation. Run 28 with the same catalyst and with a mole ratio of 5 to 1 gave a great deal of carbon. The line leading to the condensers was blocked after 8 hours of operation. Run 29 in which the mole ratio was 1 to 3 was not successful because it was not possible to analyze the off-gases from this run. The high concentration of unreacted ammonia in the off-gases resulted in too high heat of absorption and failure of the magnesium perchlorate absorbing system. An estimation of the conversion was made assuming that the liquid obtained was acetonitrile.

The data are plotted in Figure 4. Apparently a smoother reaction is obtained at lower ratios of acetylene to ammonia. The data are not sufficient to show an optimum in the curve but do show conclusively that ratios in the range of 1 to 1 are more desirable than those of 3 to 1 or 5 to 1.

INFLUENCE OF DILUTE ACETYLENE. The commercial feasibility of any process is dependent upon efficient use of available raw materials. The work on condensation of acetylene with ammonia in runs 1 through 29 was carried out using pure acetylene. Regardless of other factors influencing the condensation it is obviously advantageous to use a dilute acetylene gas, such as Wolff gas, which is relatively cheap and abundant rather than a highly concentrated acetylene. Runs 30 and 31 were made using acetylene diluted with hydrogen to see if the condensation would proceed with dilute acetylene as one of the reactants.

Run 30 was carried out at 510° C. with a catalyst containing 40 mole % zinc chloride and 60 mole % sodium chloride. The mole ratio of acetylene-ammonia-hydrogen was 1 to 2 to 5.7. After 4 hours of operation very little liquid was obtained. A higher percentage of acetylene was used in run 31. The mole ratio was 1 to 1 to 3.5 in this run. After 6 hours, 3.6 grams of liquid were obtained. The data show more ammonia out than was fed in because of absorption of product by the magnesium perchlorate, which did not condense because of its low partial pressure in the off-gas stream. By assuming that the excess ammonia was actually product, the yield from this run was 36.5%. Apparently the reaction efficiency is not as great under these conditions as in the case of some of the other runs where higher yields were obtained using pure acetylene. However, operation on a larger scale could very well show that the dilute acetylene can be used efficiently.

DISTILLATION AND IDENTIFICATION OF THE PRODUCT. The liquid product obtained in each run was fractionated individually in the column previously mentioned. In all cases a sharp break in the distillation curve occurred at 80° to 82° C. with small amounts of high boiling residue ranging from 8 to 20% by weight of the charge to the still. This heavy material had an odor characteristic of pyridine and aromatic hydrocarbons. The low boiling fractions ranging from 60° to 78° C. had an odor resembling that of diethylamine. The refractive index and density of these fractions indicated the presence of diethylamine and acetonitrile. The middle fraction, 78° to 82° C., consisted of almost pure acetonitrile and comprised over half of the product in all cases. Figure 5 is a graphical representation of the distillation data. Examination of the figure discloses that the composition of the liquid product was in general unaffected by conditions of reaction, since between 75 and 85% acetonitrile was present in all cases. Johnson and Swann (*8*) found that the character of the product by condensing acetylene in the presence of zinc chloride was essentially independent of operating conditions.

Corresponding fractions from the various runs were combined and redistilled. The analysis of this material is given in the following table.

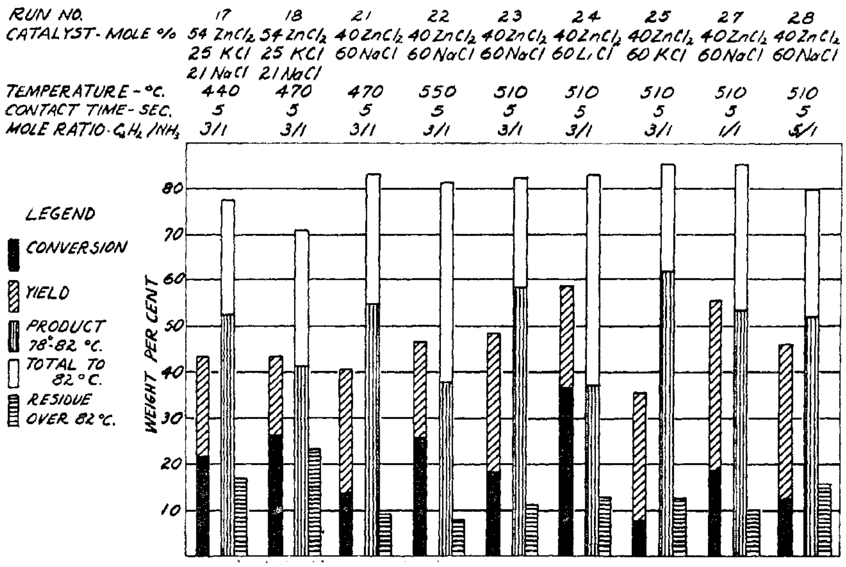

Figure 5. Composition of Liquid Products

	Diethylamine	Acetonitrile	Cut 1	Cut 2	Cut 3	Cut 4
Refractive index, n_D^{20}	1.3871	$1.3460^{16.5}$	1.3617	1.3488	1.3477	$1.3468^{16.5}$
Density, g./ml.	....	0.783	.....	....	....	0.783
Boiling pt., ° C.	56	82	74-76	76-78	78-80	82

The ethyl iminomercaptoacetic acid hydrochloride derivative made from material boiling at 82° C. had a decomposition point of 113° to 115° C. compared to 114° C. as the literature value for the corresponding acetonitrile derivative.

CONDENSATION OF ACETONITRILE WITH ACETYLENE. In the runs previously described the presence of pyridine in the product was suspected because of the pyridinelike odor of the condensate. Since pyridine was not formed as the major product, it was thought that acetonitrile might be formed first. Perhaps pyridine could be produced by means of a two-step process whereby acetonitrile would be converted into pyridine in a separate reactor. Two runs were made to test this idea. In run 32 acetonitrile, acetylene, and hydrogen were led into the reaction chamber in the correct stoichiometric ratio of 1 to 2 to 1 for the formation of pyridine by the following equation:

$$CH_3CN + 2C_2H_2 + H_2 \longrightarrow C_5H_5N + CH_4 \qquad (3)$$

The catalyst was 54 mole % zinc chloride-25 mole % potassium chloride-21 mole % sodium chloride, temperature 375° C., and contact time 5 seconds. In 4 hours of operation 49.4 grams of acetonitrile were charged, of which 43 grams were recovered unchanged. The balance was decomposed or lost as no converted product was found. The run was repeated at 510° C. At this temperature the catalyst is extremely active, leading to decomposition of the acetylene. After a short period of operation in which 8.6 grams of acetonitrile were charged, it was necessary to stop the run because of excessive carbon formation. No pyridine was detected in the products of the run.

These runs seemed to show that acetonitrile is not an intermediate in the formation of pyridine. Rather it is believed that either pyridine or acetonitrile are formed by two separate reactions either or both of which may take place. Under the conditions of this investigation the formation of acetonitrile was favored.

CONCLUSIONS

Acetylene can be condensed with ammonia in the presence of molten zinc chloride admixed with alkali chlorides as catalyst. The conversion and yield of liquid products can be influenced by the conditions under which the reaction is carried out. The composition of the liquid obtained remains essentially constant, independent of the operating conditions within the limits of the conditions of these experiments.

The catalytic activity of zinc chloride was found to be proportional to the concentration of zinc chloride in the molten salt mixtures tested. At high concentrations, overactivity of the catalyst resulted in undesirable secondary reactions leading to decomposition of the acetylene and/or reaction products. There exists at any temperature level within the range investigated an optimum concentration for smooth reaction with good conversion and minimum decomposition. At 470° C. this optimum concentration lies in the region of 40 mole % zinc chloride.

The catalytic activity of molten zinc chloride was found to be proportional to the temperature at which the condensation is carried out. For a given concentration there exists an optimum temperature of reaction favoring maximum yield of liquid product with minimum decomposition. There is a lower temperature limit with this catalyst of 430° C. below which no condensation takes place. The presence of a stable $ZnCl_2.(NH_3)_x$ complex which inhibits the catalytic activity of the zinc chloride was demonstrated. In this complex x is probably 1. The complex is unstable at temperature higher than 430° C. Above this temperature zinc chloride was found to be an active catalyst for the condensation.

The diluent alkali chlorides admixed with zinc chloride influence the activity of the zinc chloride inversely to their molecular weights. Thus lithium chloride-zinc chloride is considerably more active than potassium chloride-zinc chloride, other conditions being equal. This effect is the basis for the theory that the diluent alkali chlorides are held around the zinc chloride more or less loosely in solution, preventing the zinc chloride molecules or ions from coming in contact with the reactant gases. The effectiveness of such shielding is thought to be a function of molecule size so that the lighter lithium chloride can be considered not to promote the activity of the zinc chloride more than potassium chloride but rather to shield the zinc chloride molecules less. The alkali chlorides were not in themselves catalysts for the condensation.

A smooth reaction is promoted by low ratios of acetylene to ammonia. The best yield was obtained at a ratio corresponding to stoichiometric amounts of acetylene and ammonia for the formation of acetonitrile. Higher ratios lead to decomposition and carbon formation.

Acetylene and ammonia will condense when the acetylene is present as a dilute gas. The yield and conversions are low but appreciable.

The product of this condensation contained 75 to 85% acetonitrile, probably some diethylamine, and the remainder high boiling material probably consisting of pyridine bases and aromatic hydrocarbons.

Limited evidence is presented to show that acetonitrile is not formed as an intermediate in the formation of pyridine under the conditions employed in this investigation. Probably the condensation can proceed to form either pyridine or acetonitrile and the present conditions are favorable to the formation of acetonitrile.

The following molten salt systems were not active catalysts for the condensation under the experimental conditions tested or were not suited to the present method:

33 mole % $CdCl_2$–43 mole % KCl–24 mole % NaCl
46 mole % $PbCl_2$–38 mole % KCl–16 mole % NaCl
37 mole % $FeCl_3$–37 mole % KCl–26 mole % NaCl
50 mole % $SnCl_2$–50 mole % KCl

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Pure Hydrocarbons from Petroleum

PREPARATION OF METHYLCYCLOHEXANE FROM STRAIGHT-RUN HEPTANE FRACTION

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Constructional details and performance of the improved Distex pilot plant are given. Methylcyclohexane of high purity was prepared from a narrow-boiling straight-run fraction by four successive operations: (1) a continuous fractionation removed most of the material boiling below *n*-heptane; (2) a Distex operation eliminated nearly all of the heptane with the remainder of the lighter materials; (3) a second Distex operation eliminated the toluene with part of the higher naphthenes; and (4) a batch fractionation recovered methylcyclohexane of purity about 99 mole %.

THE principles of and general Distex procedure for obtaining pure hydrocarbons from narrow-boiling straight-run fractions have been discussed (*1*). Briefly, the method consists of separating the fraction into groups of single structural types of hydrocarbons by solvent fractionation (the Distex operation), then recovering the pure compounds by conventional fractionation of the individual groups.

In the preceding article of this series (*3*), the second Distex pilot plant was described with its application to the separation of a commercial straight-run heptane fraction (Skellysolve C) for the preparation of pure *n*-heptane.

During the course of the work, the capacity of the pilot plant column slowly but steadily decreased because of an accumulation of and clogging by sedimentlike material.

For the present work, the new column was built with removable plate sections and most of the accessories were reconstructed to avoid difficulties experienced earlier and to give higher capacity and better control of the operation.

IMPROVED PILOT PLANT

A detailed flow diagram of the pilot plant is shown in Figure 1. The construction, insulation, heat compensation, and thermocouple details of column 3 are given in an earlier article (*2*). It contained 150 removable screen plates as 50-plate sections mounted in 2-inch standard pipe, and had approximately double the capacity of the earlier column of the same diameter. (Actually, steel conduit tubing of the same dimensions was used. Each section contained two strings of 25 plates.) At the higher rates obtained, the earlier solvent recovery column proved to be of inadequate capacity. The new solvent recovery column is shown in Figure 2. The section above the feed contained six screen plates of the same design as for the main column. The

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