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The Polymerization of Acetonitrile in the Presence of Acidic and Basic Substances

By Eizo OIKAWA, Kyoichi MORI and Goro SAITO

Faculty of Engineering, Niigata University, Nagaoka, Niigata

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Complexes of saturated nitriles with metal chlorides polymerize readily. In this paper, the polymerization of acetonitrile was carried out with more nitrile, than was needed to form the complex with metal chlorides. The conversion of the polymer increased in comparison with the case of the polymerization of the complex, indicating that the complex would partly dissociated in the reaction. The trimer of acetonitrile, 4-amino-2, 6-dimethylpyrimidine, was isolated, and ammonia was detected in addition to the brown polymer. The mechanism of the trimer formation in the presence of metal chlorides was illustrated through the removal of a proton from acetonitrile with the help of the chlorides, and through dimer formation. Hydrochloric acid and metaphosphoric acid were less active than metal chlorides. Ammonia itself was found to be inactive for the trimerization, bringing only acetamide. Water was also inactive in response to acetonitrile in the absence of acidic or basic substances. The derivation of ammonia was attributed to the decomposition of the pyrimidine compound and/or to the degradation of the polymer, but not to the hydrolysis of acetamide. The reaction of the polymer with propionaldehyde, the hydrolysis of the product, the carbylamine test, and a treatment of the trimer similar to that used for the complex suggested that the pyrimidine rings are involved in the polymer structure.

In previous papers[1,2] the polymerization of complexes of saturated nitriles with metal chlorides and the structure of the polymers have been reported. The composition of complex of the nitrile (RCN) with metal chloride (MCl_n) is definite (generally $2RCN:MCl_n$). If however, the metal chlorides behave as catalysts in the polymerization, the chlorides need not necessarily be added in amounts large enough to convert the whole nitrile into the complex. In the present investigation the polymerization was carried out with the excess nitrile; in other words, more nitrile than was needed to form the complex was added to the polymerization system in order to investigate if it is valid to say that only the nitrile that forms the complex is able to polymerize, while the free nitrile in the system is not.

In the polymerization, the trimer, 4-amino-2, 6-dimethylpyrimidine, and ammonia were obtained in addition to the polymer. The formation of the trimer has briefly been reported by Kabanov et al.[3] The mechanism of these formations in the presence of acidic substances was investigated, and it was suggested that the polymers include pyrimidine rings.

Experimental

Materials and Procedure.—The materials and the procedure were the same as those described in a previous paper.[2] The nitrile was added to the metal chlorides under a nitrogen atmosphere.

The sealed tube was heated in an autoclave under

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[1] E. Oikawa and S. Kambara, *J. Polymer Sci.*, **B2**, 649 (1964).

[2] E. Oikawa and S. Kambara, This Bulletin, **37**, 1849 (1964).

[3] V. A. Kabanov, V. P. Zubov, V. P. Kovaleva and V. A. Kargin, *J. Polymer Sci.*, **C** No. 4, 1009 (1963).

the pressure of isobutyl alcohol in order to prevent the tube from breaking. After they had been heated for the required time, the dark brown mass and liquid were transferred to a sublimation apparatus. The unconverted nitrile was distilled off, and sublimation followed. The white sublimate was submitted to elementary analyses. The ratio of acetamide and the pyrimidine in the sublimate was determined from the nitrogen concent by means of the Kjeldahl method using the following equation:

$$X=(N-23.7)/0.105$$

where X is the percentage of the pyrimidine compound (%) and N is the nitrogen content of the sublimate (%).

The Reaction of the Polymer with Propionaldehyde.—In a 100-ml. three-necked flask with a stirrer, a condenser and a thermometer, 25 ml. of propionaldehyde⁽4⁾ and 0.3 g. of the pulverized polymer were placed. The reaction vessel was then heated in a water bath at 40°C, with stirring continued for 6 hr. After the propionaldehyde (b. p. 49°C) had been distilled off, the residue was washed with water and dried in a vacuum at 60°C. This specimen was subjected to infrared analysis. The hydrolysis of the reaction product was accomplished by refluxing it in a 0.1 N sodium hydroxide solution for 9 hr.

The Heat Treatment of 4-Amino-2, 6-dimethylpyrimidine with Metal Chlorides.—The pyrimidine compound was prepared by the trimerization of acetonitrile with sodium metal.⁽5⁾ The procedure was the same as that described previously.⁽2⁾ After the sublimation of the dark brown mass produced by heating, the residue was pulverized, washed with a diluted hydrochloric acid solution and water, and dried in a vacuum. For example, the heating of 1.03 g. of the pyrimidine compound with 2.38 g. of titanium tetrachloride ($[(CH_3CN)_3]/[TiCl_4]=2/3$) at 250°C for 4 hr. produced 0.50 g. of a brown solid (Found: N, 20.5%). The same treatment of 0.60 g. of the pyrimidine compound with 0.97 g. of zinc chloride for 8 hr. produced 0.24 g. of the product (Found: N, 16.6%). These products were insoluble or sparingly soluble in common organic solvents, but soluble in concentrated sulfuric acid.

Results and Discussion

The results of the polymerization with excess acetonitrile are shown in Table I.

In the same method as has been reported previously⁽1⁾ the activation energy of the polymerization at a molar ratio of $r=13.8$ was found to be about 19 kcal./mol., which is equal to the value obtained from the polymerization of the acetonitrile complex with titanium tetrachloride. The conversions in Table I show that more nitrile than was needed to form the complex was converted to the polymer. These facts indicate that the following dissociation will occur at least partially under the polymerization conditions:

$$\begin{array}{l} 2\mathrm{RCN{:}MCl}_n \rightleftarrows 2\mathrm{RCN} + \mathrm{MCl}_n \\ \quad\;\downarrow \\ 2(\mathrm{RCN})_m{:}m\mathrm{MCl}_n \rightleftarrows 2(\mathrm{RCN})_m + m\mathrm{MCl}_n \end{array}$$

The metal chlorides derived from dissociation can form a complex with free nitrile. Thus, the new complex and the undissociated complex will be converted to the polymer at the activation energy of 19 kcal./mol. The conversions in parentheses in Table I suggest that the chlorides do not have any remarkable catalytic effect.

The dark brown solutions of TA_32520 and ZA_22520 after polymerization were dried, and the residues were submitted to sublimation. A small amount of a white, crystalline substance was obtained; this was, for the most part, identified as 4-amino-2, 6-dimethylpyrimidine by a study of its melting point (179°C; 182°C⁽5⁾) and infrared spectrum and by elementary analyses (Found: C, 59.0; H, 7.4; N, 33.9. Calcd. for CH_3CN: C, 58.5; H, 7.3; N, 34.1%). This pyrimidine compound is usually prepared with basic catalysts, such as alkali metals and alkali metal alcoholates.⁽5⁾

In the polymerization of acetonitrile, there occurred the evolution of ammonia⁽2⁾; this might cause the trimerization of acetonitrile. The ammonia may be derived from the hydrolysis of acetamide with a trace of water included in the acetonitrile, or from the thermal degradation of the polymer.⁽2⁾ The influence of ammonia on the trimerization, therefore, was investigated with and without water. The results are summarized in Table II. All the system changed dark brown and produced the polymer. Sublimation isolated a fine, opaque sublimate and transparent sublimate, which were identified by their melting points as 4-amino-2, 6-dimethylpyrimidine (179°C) and acetamide (81°C) respectively. The gradual decrease in the pyrimidine compound and the increase of acetamide with the increase in water content suggest that water was consumed only to form acetamide; the evolution of ammonia by the hydrolysis of acetamide was not confirmed.

In each experiment of Table II there was the odor of ammonia. Whether or not the ammonia exerts the catalytic action for trimerization was examined by adding concentrated ammonia (28%) to the nitrile. Table III shows the results. The sublimatoin of a white crystalline substance after distilling off the excess nitrile isolated almost only acetamide, which was also identified by a study of its infrared spectrum; there was no colored substance. Hence, ammonia does not behave as a catalyst for the formation of the pyrimidine.

It is considered that not only Lewis acid but also proton donating inorganic acids like hydrochloric acid will promote the polymerization of the nitrile if the reaction is initiated by the removal of a proton from the $H^+\!-\!{}^-CH_2\!\equiv\!C\!-\!N{:}\!\rightarrow\!MCl_n$ complex. The results of the experiments adding 35% hydrochloric acid and metaphosphoric acid

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4) C. D. Hurd and R. N. Meinert, "Organic Syntheses," Coll. Vol. II, 541 (1948).

5) A. R. Ranzio and W. B. Cook, ibid., Coll. Vol. III, 71 (1951); T. L. Cairns, A. W. Larchar aad B. C. Mckusick, *J. Am. Chem. Soc.*, **74**, 5633 (1952).

are given in Table IV. Ammonia was detected, and there was a very small yield of a brown polymer. The infrared spectrum of the white sublimate revealed the formation of a small amount of the pyrimidine compound. Therefore, hydrochloric acid and metaphosphoric acid are less active in the trimerization and polymerization than are zinc chloride and titanium tetrachloride.

TABLE I. POLYMERIZATION OF ACETONITRILE (excess nitrile)

No.	CH_3CN g.	Metal chloride MCl_n, g.	Molar ratio, r $[CH_3CN]/[MCl_n]$	Temp. °C	Time hr.	Yield g.	Conversion* %
TA_1 258	2.58	$TiCl_4$ 2.2	5.4	250	8	1.66	174(64)
TA_1 2520	2.58	2.2	5.4	250	20	1.78	186(69)
TA_2 233	2.58	0.86	13.8	230	3	0.24	63(9.1)
TA_2 236	2.58	0.86	13.8	230	6	0.34	92(13)
TA_2 258	2.58	0.86	13.8	250	8	0.87	233(34)
TA_2 2514	2.58	0.86	13.8	250	14	0.93	250(36)
TA_2 2520	2.58	0.86	13.8	250	20	0.93	250(36)
TA_2 270	2.58	0.86	13.8	270	0.5	0.36	97(14)
TA_2 271	2.58	0.86	13.8	270	1	0.42	112(16)
TA_3 2520	2.58	0.14	84.7	250	20	0.27	454(11)
ZA_1 2520	2.58	$ZnCl_2$ 0.10	85.6	250	20	0.06	93(2.2)
ZA_2 2520	3.35	0.81	13.8	250	20	0.42	88(13)

* The calculation is based on the amount of the nitrile which was needed to form the complex $2CH_3CN : MCl_n$; ( ): These are based on the whole nitrile added.

TABLE II. SUBLIMATES IN POLYMERIZATIONS[a]

No.	CH_3CN g.	$ZnCl_2$ g.	H_2O g.	Molar ratio $\frac{[CH_3CN]}{[ZnCl_2]}$	Molar ratio $\frac{[H_2O]}{[CH_3CN]}$	Sublimate g.	Conversion[b] %	Pyrimidine %	Acetamide %	Odor of NH_3
ZA	3.79	0.149	0	85.6	0	0.809	21.3	71.3	28.6	yes
ZA′	4.45	0.173	0	85.6	0	0.956	21.5	73.6	26.4	yes
ZB	1.95	0.162	0	40.0	0	0.589	30.2	91.1	8.9	yes
ZB′	1.65	0.138	0	40.0	0	0.583	35.3	87.5	12.5	yes
ZC	2.76	0.108	0.0013	85.6	0.0010	0.412	14.9	54.5	45.5	yes
ZD	3.80	0.147	0.0490	85.6	0.0294	1.098	28·9	33.3	66.7	yes

a) Reaction conditions; 250°C, 20 hr.
b) This is based on the whole nitrile added.

TABLE III. REACTION OF ACETONITRILE IN THE PRESENCE OF NH_3[a]

No.	CH_3CN g.	NH_3 g.	H_2O g.	Molar ratio $\frac{[CH_3CN]}{[NH_3]}$	Molar ratio $\frac{[H_2O]}{[CH_3CN]}$	Product[b] g.	Conversion, %	N[c] %	Formation of polymer
NE	2.18	0.011	0.029	8	0.33	0.420	19.3	24.0	no

a) Reaction conditions: 250°C, 20 hr.
b) M. p. 78°C
c) CH_3CONH_2; N 23.7%

TABLE IV. REACTION OF ACETONITRILE IN THE PRESENCE OF INORGANIC ACID

No.	CH_3CN g.	Acid g.	H_2O g.	Molar ratio $\frac{[CH_3CN]}{[Acid]}$	Molar ratio $\frac{[H_2O]}{[CH_3CN]}$	Sublimate g.	Conversion, %	Odor of NH_3	Formation of polymer[b]
HF	1.58	HCl 0.009	0.016	151	0.073	0.125	7.9	yes	very little
HG	1.94	0.020	0.037	88.5	0.043	0.310	16.0	yes	very little
PH	1.57	HPO_3 0.041	0	81	0	0.015	1.0	—	very little

a) Reaction conditions: 250°C, 20 hr.
b) Conversion: $<0.2\%$

The presence of water in the system in all the above results increased the yield of acetamide. The polymer formed during the reaction time has been found to cause autocatalysis.[3] Thus, an attempt was made to carry out the reaction under the same reaction conditions (250°C, 20 hr.), adding to the system separately a little water and the polymer prepared from the complex,[2] without any acidic and basic substances. In either case neither colored product nor sublimable substance was formed, and there was no odor of ammonia. Hence, the polymer does not behave as a catalyst for the trimerization, nor does it give the pyrimidine compound by the degradation of the polymer.

Since the evolution of ammonia was always accompanied with the formation of the trimer or the polymer, it may be concluded that ammonia would probably be given by the decomposition of the pyrimidine compound and/or the degradation of the polymer.

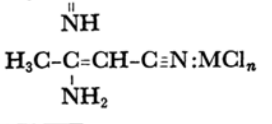
When the reaction conditions were changed from 250°C for 20 hr. to the refluxing condition for 20 hr. under an atmospheric pressure, the system of excess nitrile with zinc chloride did not give any colored product or sublimable substance. Therefore, the rise in pressure (about 30 atm. in the sealed tube at 250°C) and temperature seems always necessary. The application of high pressure (50000 atm.) and high temperature (200—400°C) to acetonitrile has brought about a similar formation of 4-amino-2, 6-dimethylpyrimidine.[6] However, the addition of metal chlorides does not need such drastic conditions, and it facilitates the trimerization and polymerization. The high conversion of the trimer with a strong basic catalyst is due to the easy removal of a proton from acetonitrile. The complex formation of the nitrile with metal chlorides may also help the removal of a proton from acetonitrile, which will in turn facilitate the following formation of a dimer and, finally, the trimer. The formation of the trimer through the dimer has been confirmed in a basic catalyst.[7]

1) Removal of a proton:

$$CH_3CN + MCl_n \rightarrow$$
$$H^+ — {}^-CH_2\text{-}C{\equiv}N\!:\!\rightarrow MCl_n$$
$$H^+ + CH_3CN \rightarrow H_3C\text{–}C^+{=}NH$$

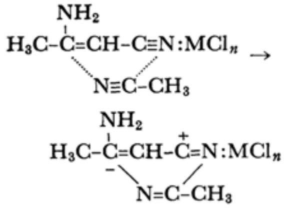
2) Formation of a dimer:

$$H_3C\text{–}C^+{=}NH + {}^-CH_2\text{-}C{\equiv}N\!:\!MCl_n \rightarrow$$

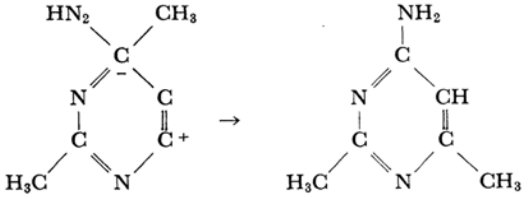


$$\underset{\overset{\|}{NH}}{H_3C\text{-}C}\text{-}CH_2\text{-}C{\equiv}N\!:\!MCl_n \rightarrow$$
$$\underset{\overset{|}{NH_2}}{H_3C\text{-}C}{=}CH\text{-}C{\equiv}N\!:\!MCl_n$$

3) Formation of a pyrimidine ring:



4) Rearrangement:



The polymer obtained in Tables I and II was similar in infrared spectra and nitrogen content to those obtained previously.[2] The polymer from the complex, when subjected to a carbylamine test, revealed positive results, while the sublimation of the polymer isolated nothing. Moreover, the infrared spectrum of a pulverized polymer suspended in propionaldehyde for 6 hr. at 40°C showed sharp new absorptions at 2850, 2920, and 2950 cm^{-1} which are probably due to C–H stretching vibrations, and a stronger absorption at 1620 cm^{-1} due to C=N. The former three absorptions disappeared upon alkaline hydrolysis. These facts support the idea that the polymer has an amino group.

The treatment of 4-amino-2, 6-dimethylpyrimidine with metal chlorides similar to that of the complex produced a dark brown solid whose infrared spectrum revealed absorptions similar to those of the polymer prepared from the complex (3400, 3000—2900 cm^{-1}: weak and broad; 1600 cm^{-1}: strong and broad). A strong odor of ammonia was found, and nothing was isolated by sublimation. The nitrogen contents of the products were comparable with those of the polymer obtained from the complex.[2]

Considering the formation of the pyrimidine compound in addition to the brown mass, it may be concluded that the pyrimidine compound takes part in the formation of the polymer as well as conjugated C–N groups.

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[6] I. S. Bengelsdorf, *J. Org. Chem.*, **28**, 1369 (1963).

[7] R. Holtzwart, *J. Prakt. Chem.*, (2) **39**, 230 (1889).