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Author(s)	Inoue, Hisayuki; Hara, Kimihiko; Osugi, Jiro
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THE REACTION OF NITRILE WITH α -HYDROGENS UNDER HIGH PRESSURE I DIMERIZATION AND TRIMERIZATION OF MALONONITRILE

BY HISAYUKI INOUE, KIMIHIKO HARA AND JIRO OSUGI

The effects of pressure on the reaction of malononitrile have been studied in water, methanol, ethanol, *iso*-propanol, dioxane, and so on in the temperature range of 323 to 343 K up to 8000 kg cm⁻²*. The reaction produced a dimer and two trimers only at high pressure. The dimer was identified as 1, 1, 3-tricyano-2-amino-1-propene and the trimers as 2, 4-diamino-3, 5-dicyano-6-cyanomethylpyridine, and ammonium 1, 1, 3, 3-tetracyano-2-cyanomethylpropenide, which are, respectively, the "Trimer 1" and "Trimer 2" reported by Schenck and Finken¹⁾. The "Trimer 3" was not yielded. 1, 3, 5-Tricyanomethyl-*s*-triazine was not produced in the present reaction either.

The polar solvents and the addition of triethylamine increased the reaction rate remarkably. The formation of the dimer is autocatalytic and its mechanism is found to be a Thorpe-type reaction.

Introduction

Most nitriles react exceedingly slowly at atmospheric pressure, unless catalysts are employed. Cairns *et al.*²⁾ have reported that the reactions of nitriles with alcohols at 343–423 K and 3–8 kbar give the corresponding *s*-triazines in the yield of 10–80%. Kurabayashi and his co-workers³⁾ elucidated the mechanism of this reaction: *s*-triazines were considered to be produced by the cyclotrimerization of the imidates formed as the intermediates from the nitriles and alcohols under pressure. Bengelsdorf⁴⁾ studied the reaction of nitriles without any solvent at very high pressure and high temperature; aromatic nitriles trimerized rather readily to the corresponding *s*-triazines; aliphatic nitriles with " α -hydrogens" afforded no *s*-triazines but polymerized. He suggested that the polymerization reaction proceeded by the Thorpe-type reaction mechanism. Although this suggestion for the reactivity of " α -hydrogens" in nitriles under such severe conditions is worthwhile indeed, the proposal for the mechanism is not based on the product analysis or other kinetic evidences. Malononitrile is one of the simple nitriles that have active α -hydrogens. Hence the mechanism of this reaction at high pressure and high temperature has been investigated thoroughly by varying solvents or by adding a

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* 1 kg cm⁻² = 0.9807 × 10⁵ Pa = 0.9807 bar

- 1) R. Schenck and H. Finken, *Ann. Chem.*, **462**, 273 (1928)
- 2) T. L. Cairns, A. W. Larchar and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 5633 (1952)
- 3) M. Kurabayashi, K. Yanagida and M. Yasumoto, *Bull. Chem. Soc. Japan*, **44**, 3413 (1971); *ibid.*, **46**, 2798, 2804, 2809 (1973)
- 4) I. S. Bengelsdorf, *J. Am. Chem. Soc.*, **80**, 1442 (1958); *J. Org. Chem.*, **28**, 1369 (1963)

catalyst.

Experimental

Apparatus

Fig. 1 shows the high pressure apparatus of piston-cylinder type used in this study. The pressure was measured in each run by means of the manganin wire gauge and the uncertainty was ± 50 kg cm⁻². A chromel-alumel thermocouple was used to measure the temperature under high pressure, and the temperature was controlled within ± 0.5 K. Silicone oil was used as pressure transmitting medium. A teflon capsule with a volume of a few milliliters was filled with the starting materials and put into the pressure vessel, the temperature of which had been already kept constant and then compressed. After the desired reaction time had passed, the pressure was rapidly reduced to the atmospheric pressure.

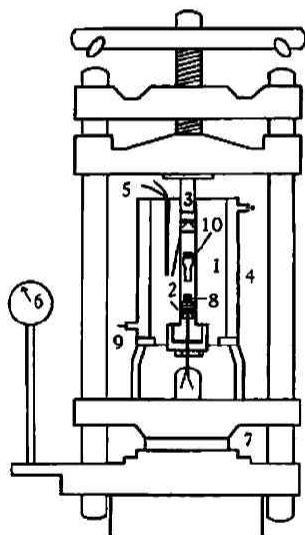


Fig. 1 Schematic diagram of apparatus
 1 Cylinder, 2 Bridgman seal, 3 Piston,
 4 Jacket, 5 Thermocouple,
 6 Bourdon gauge, 7 Ram,
 8 Manganin gauge, 9 Thermostated water,
 10 Teflon cell.

Materials

All the materials employed was supplied by Nakarai Chemicals Ltd. Malononitrile (MN) of guaranteed reagent grade was recrystallized twice from ethanol and distilled under reduced pressure (362 K/0.03 bar). Triethylamine of guaranteed reagent grade was purified by distillation (362 K). Methanol (MeOH) and ethanol (EtOH) of guaranteed reagent grade were dried with anhydrous calcium sulfate and then distilled. *iso*-Propanol (*iso*-P:OH), dioxane, acetone of chromatographic grade, ethyl ether of extra pure reagent grade, dimethyl sulfoxide-d₆, D₂O, and tetramethylsilane (TMS) of spectroscopic grade were used without further treatment. 1, 1, 3-Tricyano-2-amino-1-propene (CAP) was prepared by the reported method⁵⁾. A solution of 6.6 g (0.1 mol) of malononitrile and 4 g (0.2 mol)

5) R. A. Carboni, D. O. Coffman and E. G. Horward, *J. Am. Chem. Soc.*, **80**, 2838 (1958)

of sodium hydroxide in 25 cm³ of water was added to 25 g of cupric sulfate pentahydrate in 50 cm³ of warm water. The mixture was heated to 363 K and filtered to remove the insoluble inorganic salts. On cooling, the crude dimer was separated and recrystallized from water (m. p., 443–444 K; yield, 14%). 2, 4-Diamino-3, 5-dicyano-6-cyanomethylpyridine (ACPY) was synthesized by the established method⁶⁾. A solution of malononitrile 6.6 g (0.1 mol) and triethylamine 0.1 g (0.001 mol) in methanol 13.2 g (0.41 mol) was refluxed for 5 hr. The precipitated solid was filtered and washed with ethyl ether (yield, 7.8%). For ammonium 1, 1, 3, 3-tetracyano-2-cyanomethylpropenide (TCP) was obtained by using the method in this paper.

Results and Discussion

Analysis of products

When some product precipitated, it was filtrated with a glass filter and washed with ethyl ether into which other products dissolved well. The separation of the products soluble in ethyl ether was accomplished by passing acetone-ethyl ether (1 : 1, in volume) solution through a column of silica gel. After all, three kinds of the products were isolated. According to the elemental and the mass spectral

Table 1 Instrumental analysis of the reaction products of malononitrile

	CAP	TCP	ACPY
Elemental analysis			
H (%)	2.96	2.81	2.83
C (%)	54.00	54.16	54.03
N (%)	40.31	40.55	40.31
Mass spectrum			
P (m/e)	132	198	198
NMR spectrum ^{a)}			
ppm from TMS	3.78 (s, 2)	3.58 (s, 2)	4.12 (s, 2)
100 MHz	8.82–8.92 (b, 2)	6.52 (b, 4/3)	7.34 (b, 2)
in DMSO-d ₆		7.02 (b, 4/3)	7.52 (b, 2)
		7.52 (b, 4/3)	
IR spectrum			
cm ⁻¹	3350, 3230, 2180, 1655	3200, 2180, 1500	3400–3200, 2200, 1600
	1555, 1387, 1309, 907	1400	1560, 1500
UV spectrum			
nm	274	360	240, 328, 345
in MeOH			
Melting point			
K	444.0–445.0	497.6–499.1	>573

a) All the peaks are singlet. In the brackets, symbols s and b indicate respectively sharp and broad peaks, and the numbers the integral intensities.

6) M. Taguchi and K. Matsuura, *Yuki Gosei Kagaku Kyokaishi*, **27**, 1230 (1969)

analyses, they were supposed to be a dimer and two trimers (one trimer precipitated in ethyl ether). The dimer was identified with 1, 1, 3-tricyano-2-amino-1-propene by comparing its melting point, elemental analysis, and spectra, such as mass, NMR, UV, and IR with those of the authentic sample synthesized. The physical properties of the isolated products are shown in Table 1 and the NMR spectrum of the mixtures is shown in Fig. 2. Various structural formulas⁶⁻⁹⁾ have been proposed for

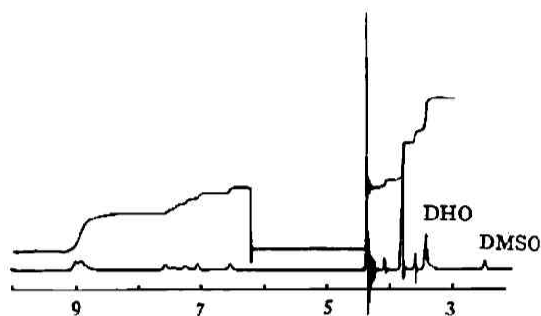


Fig. 2 NMR spectrum of the reaction products of malononitrile under high pressure in DMSO- d_6
Internal reference, TMS
Measured at 100 MHz and room temperature

trimers of malononitrile. Schenck and Finken showed three ways to synthesize the trimers which were called "Trimer 1, 2, and 3" (Fig. 3): "Trimer 1" (ACPY) was obtained by the treatment of an etha-

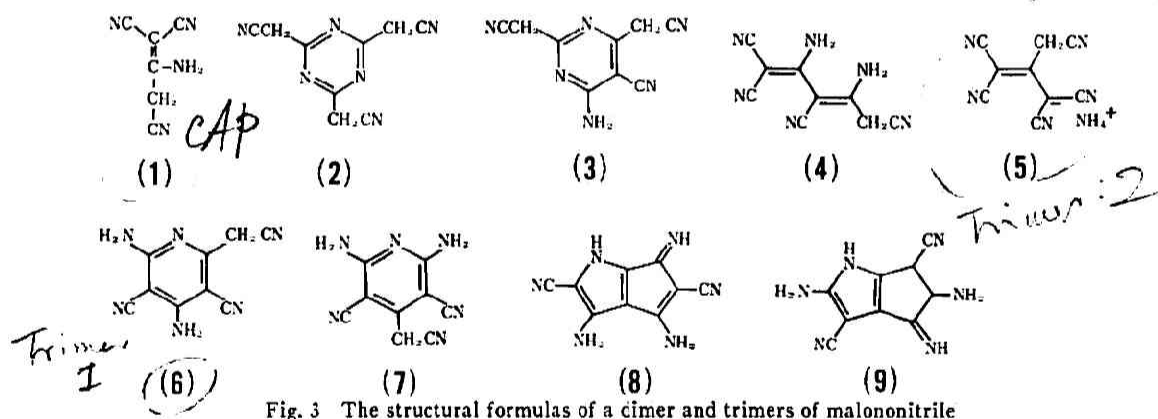


Fig. 3 The structural formulas of a dimer and trimers of malononitrile

nolic solution of malononitrile with diethylamine, "Trimer 2" from the benzene solution passing ammonia, and "Trimer 3" from the pyrolysis of "Trimer 2". Taguchi *et al.*⁶⁾ considered "Trimer 1" to have the pyridine structure (6) from the instrumental analyses, such as NMR, IR, and especially mass spectroscopy. The physical properties of the present precipitated trimer correspond well to those given by Taguchi as shown in Table 1. The molecular structure of the trimer in the liquid phase was examined by using NMR as well as the other instrumental analyses in Table 1. The NMR spectrum of the trimer in DMSO- d_6 showed four peaks at 3.58 (sharp, s), 6.52 (broad, s), 7.02 (broad, s), 7.52 (broad, s) ppm relative to TMS; the integral ratio of the peaks was 3 : 2 : 2 : 2. The three peaks in

7) D. M. W. Anderson, F. Bell and J. L. Duncan, *J. Chem. Soc.*, 4705 (1961)

8) H. Junek and H. Sterk, *Z. Naturforsch b* 22 (7), 732 (1967)

9) J. W. Ducker and M. J. Gunter, *Aust. J. Chem.*, 26, 2567 (1973)

the lower field disappeared when D₂O was added, their coupling constant being 50 Hz. The NMR data indicate that there exists a positive charge on the nitrogen atom. Hence, the structure (5), "Trimer 2" would be most reasonable for the trimer in the liquid phase.

The "Trimer 3" was not produced under the present conditions studied. The temperature attained in the present investigation seems insufficient for the activation energy of the thermal isomerization of "Trimer 2" to "Trimer 3".

Time dependence of the yields

The yield* of each product was determined by using the NMR peaks corresponding to the methylene protons. The variation of the composition of the products with time measured under various conditions is shown in Tables 2-1~9 and Figs. 4-1, 4-2 and 4-3. As can be seen in Figs. 4-2, 4-3, CAP, TCP and ACPY are formed successively at high pressure and high temperature, and their rates of formation are accelerated by pressure and/or temperature, though they are not yielded at normal

Table 2-1~9 Time dependence of the composition of the reaction products
2-1 [MN]₀ = 7.57 mol kg⁻¹ in MeOH at 1 kg cm⁻² and 333 K

Products	MN	CAP	TCP	ACPY	OP ^{a)}
<i>t</i> /hr = 8 ^{b)}	100	0	0	0	0

a) Other products

b) Reaction time

2-2 [MN]₀ = 7.57 mol kg⁻¹ in MeOH at 5000 kg cm⁻² and 343 K

Products	MN	CAP	TCP	ACPY	OP
<i>t</i> /hr = 1	100	0	0	0	0
2	95.9	4.1	0	0	0
3	92.5	7.5	0	0	0
4	88.5	11.5	0	0	0
5	81.5	18.5	0	0	0
6	72.6	26.5	0.9	0	0
7	61.0	36.9	2.1	0	0
8	45.0	45.8	6.9	2.3	0

2-3 [MN]₀ = 7.57 mol kg⁻¹ in MeOH at 6000 kg cm⁻² and 343 K

Products	MN	CAP	TCP	ACPY	OP
<i>t</i> /hr = 1	100	0	0	0	0
2	93.2	6.8	0	0	0
3	83.8	16.2	0	0	0
4	75.4	20.1	3.0	1.5	0
5	65.3	28.3	6.2	0.2	0
6	42.8	36.6	10.8	9.8	0

* Theoretical yield based on malononitrile

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2-4 $[MN]_0 = 7.57 \text{ mol kg}^{-1}$ in MeOH at 7000 kg cm^{-2} and 343 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 0.5$	100	0	0	0	0
1	96.1	3.9	0	0	0
2	82.4	14.1	3.5	0	0
3	73.5	20.2	6.3	0	0
4	60.6	30.0	7.3	2.1	0
5	33.0	36.3	15.7	10.0	5.0
6	2.0	39.5	25.6	15.7	17.2

2-5 $[MN]_0 = 7.57 \text{ mol kg}^{-1}$ in MeOH at 8000 kg cm^{-2} and 343 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 0.5$	95.4	4.6	0	0	0
1	89.1	10.9	0	0	0
2	71.5	22.0	6.3	0.2	0
3	33.0	30.3	16.8	7.6	12.3

2-6 $[MN]_0 = 7.57 \text{ mol kg}^{-1}$ in MeOH at 6000 kg cm^{-2} and 333 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 1$	100	0	0	0	0
2	97.5	2.5	0	0	0
3	96.3	3.7	0	0	0
4	94.1	5.9	0	0	0
5	90.3	9.7	0	0	0
6	83.0	17.0	0	0	0

2-7 $[MN]_0 = 7.57 \text{ mol kg}^{-1}$ in MeOH at 6000 kg cm^{-2} and 323 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 1$	100	0	0	0	0
2	100	0	0	0	0
3	98.3	1.7	0	0	0
4	98.0	2.0	0	0	0
5	97.3	2.7	0	0	0
6	96.6	3.4	0	0	0

2-8 $[MN]_0 = 5.26 \text{ mol kg}^{-1}$ in EtOH at 6000 kg cm^{-2} and 343 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 1$	100	0	0	0	0
2	98.2	1.8	0	0	0
3	95.9	4.1	0	0	0
4	93.5	6.5	0	0	0
5	90.4	9.6	0	0	0

2-9 $[MN]_0 = 5.26 \text{ mol kg}^{-1}$ in EtOH at 7000 kg cm^{-2} and 343 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 1$	100	0	0	0	0
2	97.6	2.4	0	0	0
3	93.4	6.6	0	0	0
4	88.3	11.7	0	0	0
5	80.1	19.9	0	0	0

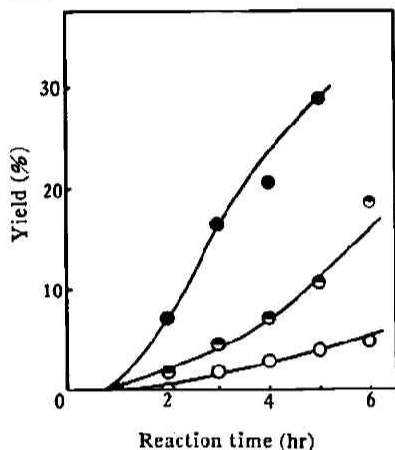


Fig. 4-1 Time and temperature dependence of CAP formation in MeOH at 6000 kg cm^{-2} , $[MN]_0 = 7.57 \text{ mol kg}^{-1}$
 ○: 323 K, ◐: 333 K, ●: 343 K

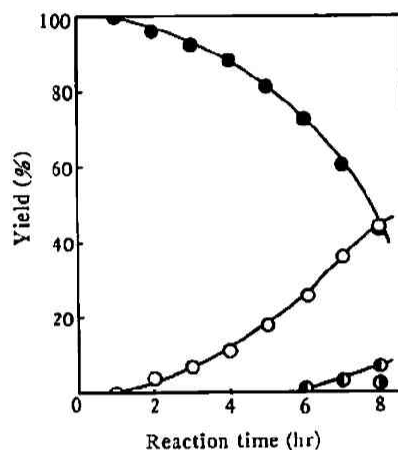


Fig. 4-2 Time dependence of the yield of the reaction products in MeOH at 5000 kg cm^{-2} and 343 K
 ●: MN, ○: CAP, ◐: TCP, ◑: ACPY

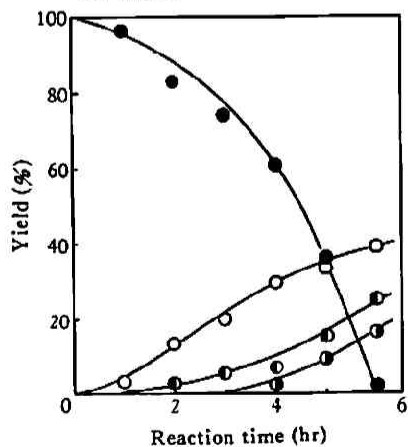


Fig. 4-3 Time dependence of the yield of the reaction products in MeOH at 7000 kg cm^{-2} and 343 K
 ●: MN, ○: CAP, ◐: TCP, ◑: ACPY

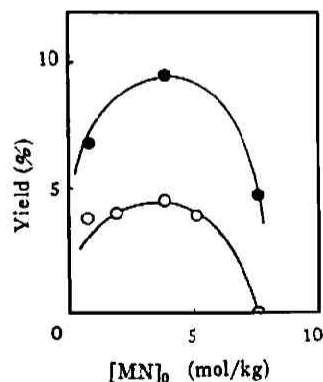
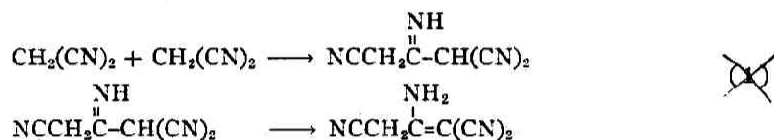


Fig. 5 Change of CAP yield against the starting concentration of MN in MeOH after 1 hr at 343 K under high pressure
 ○: 6000 kg cm^{-2} , ●: 7000 kg cm^{-2}

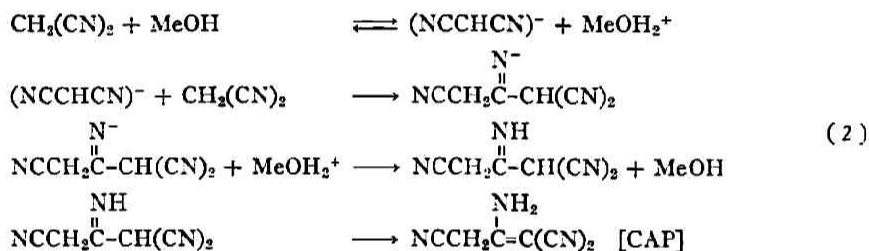
pressure and temperature. The rate of production of CAP increases after the appearance of itself; the curve of the yield *vs.* time where TCP and ACPY are not formed is convex downward, which is characteristic of autocatalytic reaction. It is to be noted that the rate of CAP formation has a tendency to slow down after its yield reaches a certain value: $\sim 37\%$ at 5000 kg cm^{-2} and 343 K ; $\sim 28\%$ at 6000 kg cm^{-2} ; $\sim 25\%$ at 7000 kg cm^{-2} ; $\sim 22\%$ at 8000 kg cm^{-2} . The drop of CAP formation can be ascribed to the consumption of CAP by the trimer formation as discussed below.

Reaction mechanism

Two different cases are considered as the initiation. The first is a kind of the one step formation of the imin type of CAP, and it rearranges fast to the enamine type of CAP;



The other is a multi step one with methanol as a catalyst:



or

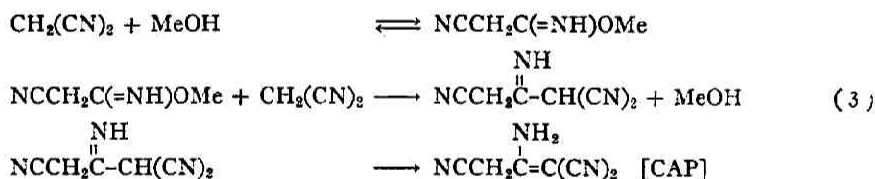


Fig. 5 shows that there is a maximum at about 3.5 mole kg^{-1} in the curve of the decreasing rate of malononitrile against the molar concentration of malononitrile. This fact may be explained by the rate equation of the following type,

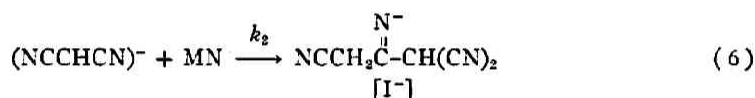
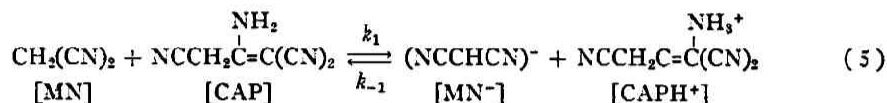
$$-d[\text{MN}]/dt = k[\text{MN}]^m[\text{MeOH}]^n. \quad (4)$$

Therefore, the step (1) considered above would be inferior to the second one.

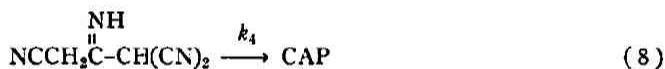
The dimers and trimers of nitriles were usually synthesized with an acid or a base catalyst at atmospheric pressure: base catalysts give the dimers and trimers having a pyridine or a pyrimidine ring; acid catalysts give the trimers, trisubstituted-*s*-triazines¹⁰⁾. By using high pressure Cairns *et al.*²⁾

10) K. Wakabayashi, *Bull. Chem. Soc. Japan*, **42**, 2924 (1969); F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961)

succeeded in preparing *s*-triazines from many kinds of nitriles with or without α -hydrogens in much higher yields than those even obtained at atmospheric pressure. Judging from the kinds of the products, methanol appears to act as an acid catalyst under the condition. According to the present high pressure experiments, malononitrile with very active α -hydrogens (pK_a of $\text{CH}_2(\text{CN})_2=11.2^{11)}$, pK_a of $\text{CH}_2\text{CN}=\sim 25^{12)}$ does not yield the corresponding *s*-triazine but the dimer, CAP and the other trimers, TCP and ACPY. All of these products seem to suggest that the reaction of malononitrile at high pressure occurs by the mechanism of a basic catalyst. Malononitrile reacts with the aid of basic catalysts at atmospheric pressure¹³⁾, and the mechanism is considered as follows:



and



The reactions (5) and (6) would be enhanced to a large extent by increasing pressure, because the reaction (5) produces ions and the reaction (6) is accompanied by a decrease in the intrinsic volume. Consequently, the immense acceleration of the reaction of malononitrile by pressure would be accounted by this Thorpe reaction mechanism, if either of the reactions (5) and (6) is a rate-determining step. Furthermore, since the amino group in CAP has a possibility to act as a base to unreacted malononitrile, this reaction can proceed autocatalytically as pointed out above.

It has been widely accepted⁹⁾ that the nitrile trimerizes into the trisubstituted-*s*-triazine *via* the iminoether or amidine: the reversible iminoether or amidine formation reaction is accelerated by increasing pressure, decreased progressively in the order of methanol, ethanol, propanol, *iso*-propanol, and promoted¹⁴⁾ by the presence of electron-attracting groups in the nitrile. Although the present reaction of malononitrile gives no *s*-triazine, an analogous mechanism may be apparently supposed for the reaction of malononitrile as follows: through the iminoether, $\text{NCCH}_2\text{C(=NH)OR}'$,

11) R. P. Bell, "The Proton in Chemistry" Cornell University Press, Chap. 6, Ithaca, New York (1959)

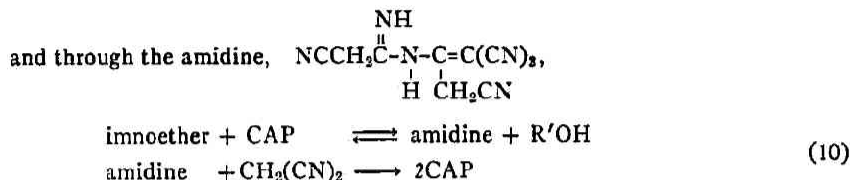
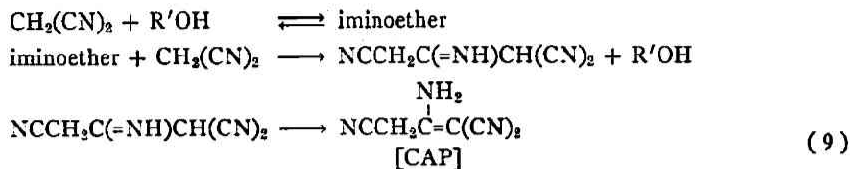
12) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953)

13) H. Baron, F. G. P. Remfry and J. F. Thorpe, *J. Chem. Soc.*, **85**, 1726 (1904); F. S. Eberts, G. Somp and J. L. Johnson, *Arch. Biochem. Biophys.*, **95**, 305 (1961)

14) N. S. Bayliss, R. L. Heppollette, L. H. Little and J. Miller, *J. Am. Chem. Soc.*, **78**, 1978 (1955); F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961)

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It may be explained in terms of the first mechanism (reactions (5), (6), (7) and (8)) or the second (reactions (9) and (10)) that the reaction of malononitrile is enhanced markedly by pressure and shows an autocatalytic feature. However, the following experimental results hardly support the second mechanism: 1) as shown in Table 2, the reaction really occurred rapidly in water and in dioxane as well as in alcohols³⁾, the reaction rate being in the order, water, methanol, ethanol, *iso*-propanol, and dioxane; 2) when the solvent polarity increases as in Tables 3 (pure solvents) and 4 (mixed solvents),

Table 3 Yield of CAP in various solvents after 3 hr at 6000 kg cm⁻² and 343 K

Solvents	H ₂ O	MeOH	EtOH	<i>iso</i> -PrOH	Dioxane
CAP (%)	17.2	16.2	4.1	~0	~0

The mole fraction of MN is 0.024 in water and 0.193 in other solvents

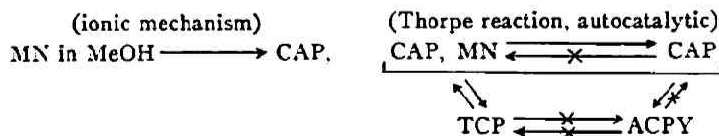
Table 4 Yields (%) of the reaction products of MN in mixed solvents at 6000 kg cm⁻² and 343 K

[MN] ₀ and Products	[MN] ₀ ^{a)}	MN	CAP	TCP	ACPY
MeOH + H ₂ O (0.905) ^{b)}	1.87	43.3	39.4	~0	0
MeOH + DMSO-d ₆ (0.972)	1.89	91.1	8.9	0	0
MeOH (1)	2.00	95.7	4.3	0	0
MeOH + Dioxane (0.709)	3.97	~100	~0	0	0

a) mol kg⁻¹

b) mole fraction of MeOH

the reaction becomes faster, which is a sign of the existence of an ionic reaction mechanism; 3) the reaction in dioxane with triethylamine* which gives no amidines proceeds rather slowly at 1 atm, and in much higher velocity at 4000 kg cm⁻² and 343 K. Based on the discussions above and below, the following scheme can be drawn for the reaction of malononitrile in methanol at high pressure and high temperature:



* It is well known that amidines are formed from imidates, so that the reaction (2) would be more probable than the reaction (3) as the initiation process.

The reversibility of each step in the above reaction scheme was examined by carrying out the same high pressure experiments on the isolated products as shown in Tables 5-1 and 5-2. When the results

Table 5-1 The reversibility of the isolated products in MeOH at 343 K under high pressure

Product (%)	MN	CAP	TCP	ACPY
MN ^{a)}	60.7	32.1	5.4	1.8
CAP ^{b)}	~0	~100	~0	~0
TCP ^{c)}	0.2	26.5	70.1	3.2
ACPY ^{d)}	0	0	0	100

a) $[MN]_0 = 3.78 \text{ mol kg}^{-1}$, after 3 hr at 6000 kg cm^{-2}

b) $[CAP]_0 = 0.98 \text{ mol kg}^{-1}$, after 3 hr at 6000 kg cm^{-2}

c) $[TCP]_0 = 0.98 \text{ mol kg}^{-1}$, after 4 hr at 7000 kg cm^{-2}

d) $[ACPY]_0 = 1 \text{ mol kg}^{-1}$, after 4 hr at 7000 kg cm^{-2}

Table 5-2 Time dependence of reaction products at the starting ratio of MN : CAP : MeOH = 1 : 0.046 : 2 (mol) at 6000 kg cm^{-2} and 343 K

Products	MN	CAP	TCP	ACPY	OP
$t/\text{hr} = 0$	95.4	4.6	0	0	0
1	84.0	16.0	0	0	0
2	71.6	22.5	4.5	1.4	0
3	63.7	25.7	9.0	1.6	0
4	52.8	29.1	13.1	5.0	0
5	33.0	35.5	20.5	11.0	~0

in the second and the fourth row of Table 5-1 are compared, it would be concluded that a small amount of ACPY did not come directly from TCP but through the state where CAP, MN and others may exist. Furthermore, the trimers seem to be formed not from CAP only, but from CAP, MN and others, according to the data in Tables 5-1 and 2-3.

Since after the time when trimers begin to be detected by NMR the reproducibility is poor, the reaction mechanism is ambiguous, and only the kinetics of the reactions (5), (6), (7) and (8) is considered here. Applying the stationary-state approximation to MN^- and I^- , the rate equation (11) can be obtained;

$$\frac{d(\text{CAP})}{dt} = \frac{k_1 k_2 (\text{CAP})(\text{MN})^2}{k_{-1}(\text{CAPH}^+) + k_2(\text{MN})} \quad (11)$$

If $k_2(\text{MN}) \gg k_{-1}(\text{CAPH}^+)$, we have from Eq. (11),

$$\frac{d(\text{CAP})}{dt} = k_1(\text{MN})(\text{CAP}) \quad (12)$$

If the following equations.

$$k_{-1}(\text{CAPH}^+) \gg k_2(\text{MN}), \quad (13)$$

and

$$(\text{CAPH}^+) = (I^-) + (\text{MN}^-) \approx (\text{MN}^-), \quad (14)$$

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can be assumed furthermore, we get,

$$d(\text{CAP})/dt = k_2(k_1/k_{-1})^{1/2}(\text{CAP})^{1/2}(\text{MN})^{3/2}, \quad (15)$$

In an early stage of the reaction, Eqs (12) and (15) can be integrated approximately. The plot of the concentration of CAP against time has been better fitted by the integrated form of Eq. (12). Hence the proton transfer from MN to CAP would be the rate-determining step, as sometimes can be seen in aldol condensation reactions. The rate constants obtained thus under the various conditions (5000 ~ 8000 kg cm⁻², 323~343 K) are listed in Table 6. From these values, the activation parameters have been calculated: $\Delta V^\ddagger = -15 \text{ cm}^3 \text{ mol}^{-1}$, $\Delta H^\ddagger = 4 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = 7.4 \text{ JK}^{-1} \text{ mol}^{-1}$.

Table 6 Rate constant of autocatalytic CAP formation

P (kg cm ⁻²)	T (K)	$[\text{MN}]_0$ (mol kg ⁻¹)	Solvent	$k \times 10^5$ (kg mol ⁻¹ s ⁻¹)
5000	343	7.57	MeOH	2.15
6000	343	7.57	MeOH	3.58
7000	343	7.57	MeOH	6.08
8000	343	7.57	MeOH	10.6
6000	333	7.57	MeOH	1.63
6000	323	7.57	MeOH	0.74
6000	343	5.26	EtOH	3.58
7000	343	5.26	EtOH	4.97

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*Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606
Japan*