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The Reaction of Nitriles under High Pressure. I. The Formation of Triphenyl-1,3,5-triazine *via* the Equilibrium among Benzonitrile, Alcohols, and Benziminoethers[1]

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Benziminoethers were formed from benzonitrile and alcohols to the equilibrium extent, and then 3 mol of benziminoethers were reacted with each other to afford triphenyl-1,3,5-triazine at 2—10 kbar and 100—120°C. The equilibrium shifted toward benziminoether with an increase in the pressure. The equilibrium constant decreased progressively in the order of methanol>ethanol≈*n*-propanol≈*n*-butanol> isopropanol≈*sec*-butanol, which accords with the increasing number of substituents on the α-position of the alcohols. The formation of triphenyl-1,3,5-triazine obeyed the second-order reaction mechanism and was also retarded in the same order. The reaction was found to proceed in the following manner: Benziminoethers produced by the addition of alcohols to benzonitrile dimerize through a rate-determining step and then trimerized into triphenyl-1,3,5-triazine. The apparent activation volume of the formation of triphenyl-1,3,5-triazine amounted to -31 cm^3 mol^{-1} at 110°C when methanol was used as the alcohol. The accelerating effect of the pressure on the formation of triphenyl-1,3,5-triazine is concluded to be mainly caused by the shift of equilibrium toward benziminoether. Three isomers of cyanopyridine were converted in good yields into the corresponding triazines under high pressure.

It is known that nitriles with active hydrogen on the α-position trimerize into trisubstituted-*s*-triazines *via* iminoethers (IE)[2] or amidines.[3] In 1950, Cairns[4] treated many kinds of nitriles with lower alcohols at 70—150°C and 3—8 kbar and thus obtained *s*-triazines in yields of 10—80%. He showed also that the lower the alcohol used the greater the promoting effect. In spite of these interesting findings, he did not describe the mechanism of the reaction nor the role of alcohols, although it had been known that the formation of IE from several alcohols and nitriles is reversible in the presence of alcoxide under atmospheric pressure.[5]

In our first attempt to investigate the reaction of nitriles under high pressure, benzonitrile was chosen as a representative nitrile. The equilibrium constants among benzonitrile, several alcohols, and their iminoethers were determined under high pressure, and the mechanism of the formation of triphenyl-*s*-triazine (TPT) was examined.

Results and Discussion

When the initial ratio of methanol to benzonitrile was widely varied (see Table 1), the plot of the concentration[6] of methylbenziminoether (MBI) against the benzonitrile concentration × methanol concentration gave straight lines (see Fig. 1). This fact indicates the existence of an equilibrium among benzonitrile, methanol, and MBI such as is described beolw;

$$C_6H_5CN + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5C(NH)OR \qquad (1)$$

$$K = k_1/k_2 = [IE]/[C_6H_5CN][ROH], \qquad (2)$$

where k_1 and k_2 are the rate constants for the forward and reverse reactions respectively. The equilibrium constant, K, was determined from Fig. 1 as 0.097 and 0.043 mol^{-1} l at 100°C with methanol under pressures of 7850 and 6000 kg/cm^2 respectively. Figure 2 shows that this equilibrium was established less than ten hours after the initiation of the run with methanol at 100°C and at about 8000 kg/cm^2 and not affected by the progress of the formation of TPT.

The experimental results with several lower alcohols are listed in Table 2. Fairly good agreements are seen between the K values in the right and left small columns, illustrating that the equilibria of Eq. (1) were established with these lower alcohols as well as with methanol under the reaction conditions noted in the table. Though Eq. (1) is a quasi-equilibrium reaction succeeded by the trimerization of IE (mentioned later), it is thought that the K values referred to in this paper agree, within the limits of experimental error, with those of the ideal equilibrium state influenced by no other reaction. K decreased conspicuously when methanol was replaced by ethanol, or when *n*-propanol was replaced by isopropanol. However, the replacement of ethanol by *n*-propanol or *n*-butanol or the replacement of isopropanol by *sec*-butanol did not change the constant appreciably. No IE was produced with *t*-butanol. This fact can easily be understood if one asumes that the forward reaction in Eq. (1) is more strongly retarded by the increasing substitution (either methanol or primary or secondary or tertiary) at the α-position of alcohol than is the reverse reaction.

The natural logarithms of the values of K listed in Tables 2 and 3 are plotted against the pressure and are

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1) Presented in part at the 12th Meeting of the High-pressure Symposium, Hiroshima, October, 1970.

2) F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2778 (1961); A. Yakubovich, *Chem. Abst.*, **58**, 526, 1256, 13257 (1963); *ibid.*, **62**, 562 (1965).

3) F. C. Scharfer, I. Hechenbleikner, G. A. Peters, and V. P. Wystrach, *J. Am. Chem. Soc.*, **81**, 1466 (1959).

4) T. L. Cairns, N. W. Larchar, and B. C. McKusick, *J. Amer. Chem. Soc.*, **74**, 5633 (1952), U. S. 2503979 (1950).

5) E. K. Marshall and S. F. Acree, *Am. Chem. J.*, **49**, 127 (1913); F. C. Scharefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).

6) For the calculation of the concentrations, the volume of the reaction medium was assumed to be the sum of the apparent volume of benzonitrile, alcohol, and IE, which were calculated by dividing their quantities as determined in the reaction medium by their specific gravities at 20°C. Under atmospheric pressure, the additivity in volume was found to be nearly constant for mixtures of benzonitrile, methanol, and MBI.

TABLE 1. EFFECT OF THE RATIO OF BENZONITRILE AND METHANOL[a)]

7850 kg/cm²				6000 kg/cm²			
$C_6H_5CN:CH_3OH$ (mol)	Yields (%)[b)]			$C_6H_5CN:CH_3OH$ (mol)	Yields (%)		
	C_6H_5CN	MBI[c)]	TPT[c)]		C_6H_5CN	MBI	TPT
1:79.3	26.5	55.7	7.09	1:61.6	44.8	35.8	2.33
1:39.1	22.7	56.1	15.1	1:29.8	42.2	38.6	6.75
1:25.5	25.2	53.5	19.6	1:18.2	44.1	41.7	8.28
1:19.2	20.1	51.1	25.9	1:12.8	43.5	39.1	13.0
1:12.1	19.1	46.0	31.8	1: 9.64	41.5	37.3	15.3
1:12.2	18.8	46.0	32.0	1: 7.48	42.5	35.7	17.5
1: 8.87	21.3	42.7	36.2	1: 4.78	42.3	31.9	22.9
1: 7.26	17.5	41.4	40.4	1: 3.21	46.2	29.0	21.4
1: 4.66	18.9	45.3	39.8	1: 2.16	52.0	22.5	21.5
1: 3.22	20.7	43.6	37.8	1: 1.42	67.2	19.8	8.56
1: 1.97	28.8	40.0	30.9	1: 0.825	80.7	14.5	1.54
1: 1.29	49.7	34.3	12.8	1: 0.360	89.6	7.53	1.68
1: 0.987	62.3	31.5	9.09				
1: 0.651	69.3	22.4	3.48				
1: 0.328	87.2	13.5	0.55				

a) Reaction conditions: 120°C, 10 hr.
b) Theoretical yield based on benzonitrile.
c) Abbreviations of methylbenziminoether and triphenyl-1,3,5-triazine respectively.

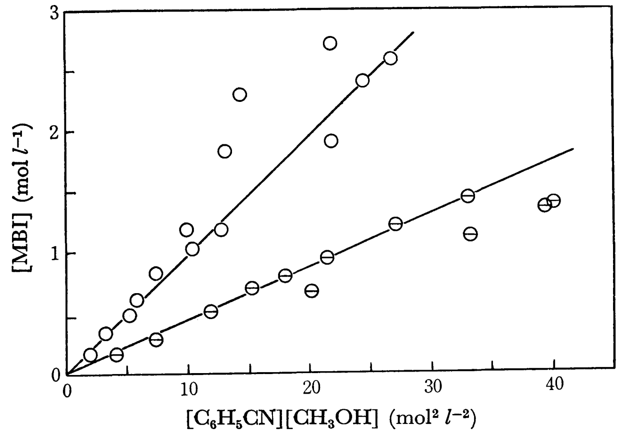

Fig. 1. Relation among the concentrations of components at 10 hr after the initiation of the reaction in the various molar ratio of C_6H_5CN: CH_3OH at 120°C.
○, 7850 kg/cm²; ⊖, 6000 kg/cm².
Deviation from the lineality seems to appear in the range of relatively high yield of TPT. The three points markedly deviating from the 7850 kg/cm² line all belongs to the runs yielding more than 35% of TPT.

shown in Fig. 3. The change in the volume (ΔV) in Eq. (1) is given by the thermodynamic equation for the liquid phase, $\partial \ln K/\partial P = -\Delta V/\boldsymbol{R}T$, and was found, by applying the tangential method to the curves in Fig. 3, to be −17.9 ml mol^{-1} at 120°C and 1 atm. This value is approximately equal to the calculated volume difference, −16.5 ml mol^{-1}, which is the difference between the sums of the molar volumes of the reactants (left side) and the product (right side) of Eq. (1) at 120°C.

The apparent rate of the formation of TPT, v_m (in mol l^{-1} hr^{-1}) is given by:

$$v_m = x/tV_m, \tag{3}$$

where x is the amount of TPT (in mol) produced in

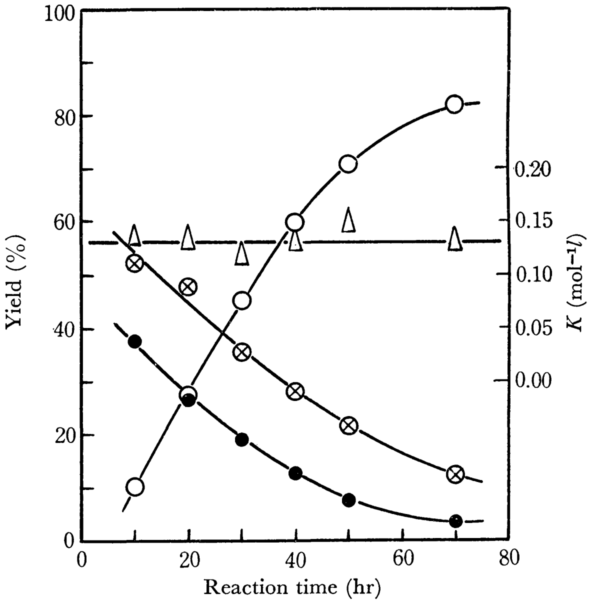

Fig. 2. Time dependence of the composition of the reaction products at the starting ratio of C_6H_5CN: CH_3OH=1: 3.2 (in mol) at 7850 kg/cm² and 100°C.
●, C_6H_5CN; ⊗, MBI; ○, TPT; △, Equilibrium constant, K=[MBI]/[C_6H_5CN][CH_3OH]

the reaction time, t (in hr), and where V_m is the mean volume of the reaction medium (in l), that is, the arithmetic mean of the initial volume[7)] and the volume at time t.[6)] The curve with open circles in Fig. 4 shows the lnv_m values plotted against the reaction pressure; it indicates a marked positive effect of the pressure on the production of TPT. From the thermodynamic equa-

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[7)] The initial volume was obtained by summing the volumes of the components at the initial point, which were calculated from the experimentally-obtained value of K and the starting amounts of the reactants.

TABLE 2. EFFECT OF ALCOHOLS ON THE EQUILIBRIUM CONSTANT, $K=[IE]/[C_6H_5CN][ROH]$[a]
The K value in the left small column of each alcohol in the large column indicates the equiriblium constant obtained for a mixture of alcohol and benzonitrile, and the K value in the right small column indicates the constant obtained for a mixture of the same alcohol and its benziminoether (IE).

Reaction conditions		8000 kg/cm², 100°C, 10 hr						8000 kg/cm², 120°C, 10 hr					
R-OH		CH_3–		C_2H_5–		n-C_3H_7–		CH_3–		C_2H_5–		n-C_3H_7–	
Reactants	C_6H_5CN	2.450	0.046[b]	2.005		1.643	0.030[b]	2.487	0.045[b]	1.955		1.651	0.031[b]
(g)	ROH	2.282	1.693	2.685	1.898	2.904	2.050	2.331	1.684	2.624	1.899	2.893	2.105
	IE		3.490		2.936		2.606		3.421		2.944		2.764
Yields (%)	C_6H_5CN	37.2	35.3	65.8	61.7	89.1	58.1	32.5	30.5	69.5	67.5	74.5	68.8
	IE	52.8	53.7	34.6	30.9	8.27	39.2	40.6	40.4	28.2	27.3	23.7	24.6
	TPT	8.69	11.4	0.57	6.84	0.10	3.43	28.1	30.1	3.15	7.71	1.21	4.67
K (mol^{-1}l)$\times 10^{-2}$		11.8	11.5	4.95	4.46	—[c]	—[c]	9.65	9.57	3.70	3.59	3.09	3.34

Reaction conditions		8000 kg/cm², 120°C, 72 hr									
R-OH		n-C_3H_7–		iso-C_3H_7–		n-C_4H_9–		sec-C_4H_9–		t-C_4H_9–	
Reactants	C_6H_5CN	1.533	0.027[b]	1.519		1.258	0.011[b]	1.305	0.006[b]	1.959	
(g)	ROH	2.729	1.884	2.656	1.805	2.800	1.995	2.817	1.969	4.224	
	IE		2.413		2.326		2.374		2.324		
Yields (%)	C_6H_5CN	64.3	56.3	81.6	69.5	63.3	48.7	89.0	85.1	(100)	
	IE	19.6	16.8	8.98	8.85	22.9	18.6	7.62	8.03		
	TPT	12.5	23.6	4.06	19.4	11.2	28.7	1.72	4.35		
K (mol^{-1}l)$\times 10^{-2}$		3.31	3.09	1.21	1.25	4.64	4.62	1.12	1.12		

Reaction conditions		5000 kg/cm², 120°C, 240 hr											
R-OH		CH_3–		C_2H_5–		n-C_3H_7–		iso-C_3H_7–		n-C_4H_9–		sec-C_4H_9–	
Reactants	C_6H_5CN	1.958	0.036[b]	1.631		1.399	0.024[b]	1.328		1.197	0.009[a]	1.240	0.006[a]
(g)	ROH	1.854	1.357	2.187	1.523	2.451	1.639	2.381	1.765	2.584	1.602	2.675	1.734
	IE		2.675		2.357		2.129		2.146		1.905		2.069
Yields (%)	C_6H_5CN	17.0	14.9	71.5	67.2	75.4	73.0	89.1	90.4	74.5	70.9	91.7	90.9
	IE	11.2	10.7	8.88	8.42	8.74	9.09	3.97	4.24	10.8	9.60	3.56	3.60
	TPT	66.9	69.4	14.9	24.1	11.5	14.2	1.97	5.42	12.4	18.3	1.12	2.19
K (mol^{-1}l)$\times 10^{-2}$		3.38	2.71	1.00	0.979	1.26	1.31	0.484	0.500	1.80	1.66	0.488	0.500

a) Reaction conditions: $C_6H_5CN:ROH=1:3.2$ (in mol).
In the right small column of each alcohol in large columns, the yields were based on benzoyl group.
b) These figures are the calculated values of benzonitrile contained as the impurities in each iminoethers.
c) The reaction time is thought to be deficient for the establishment of the equilibrium state in both or either of the two runs.

TABLE 3. EFFECT OF PRESSURE[a]

Reaction pressure (kg/cm²)	Yields (%)			K (mol^{-1}l)$\times 10^{-2}$
	C_6H_5CN	MBI	TPT	
10200	9.94	36.3	54.9	22.0
9160	18.3	45.0	36.9	16.7
7850	33.9	50.3	17.7	11.4
6620	51.3	44.8	7.14	6.96
5500	66.0	31.1	2.82	3.65
4400	81.4	19.4	0.87	1.81
3350	84.4	14.8	0.36	1.31
2340	92.4	9.23	0.0	0.774
1000	95.5	4.33	0.0	0.365
4	98.1	2.31	0.0	0.171
4[a]	97.6	2.03	0.0	0.150

a) Reaction conditions: 110°C, 10 hr, $C_6H_5CN:CH_3OH=1:3.2$ (in mol).
b) The reaction was carried on for 96 hr in a glass syringe.

tion, $\partial \ln k/\partial P=-\Delta V^{\neq}/\boldsymbol{RT}$, the apparent activation volume for the formation of TPT from benzonitrile in the presence of methanol was calculated to be -31.0 ml mol^{-1} at 110°C and 3000—5000 kg/cm². The value of v_m decreased with an increase in the number of substitution on the α-position of the alcohol added, and decreased with an increase in the number of the carbon atoms in the alkyl substituents.

The yield of TPT prepared from a mixture of an alcohol and the benziminoether of the alcohol was larger than that prepared from a mixture of the alcohol and benzonitrile (see Table 2). This fact indicates that IE plays an important role in the formation of TPT. At lower initial mixing ratios of benzonitrile to methanol, a linear relation was obtained between v_m and $[IE]_m^2$[8] as shown in Fig. 5, indicating that

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[8] $[IE]_m$ is the average value of the concentration of IE at the initial point[7] and after the reaction time t[6].

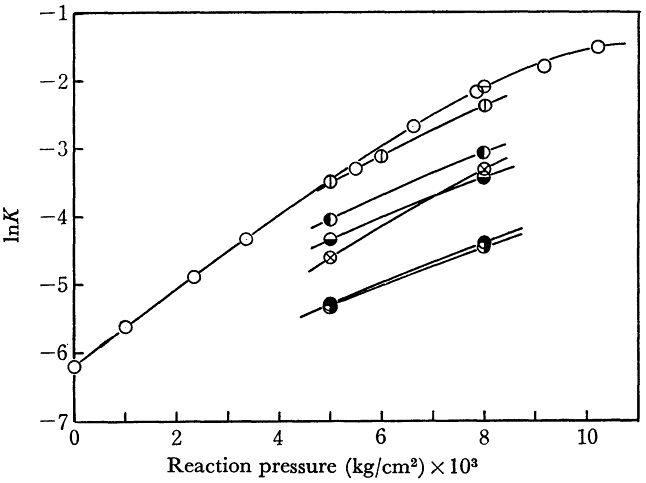


Fig. 3. Plots of the natural logarithm of equilibrium constant K listed in Table 2 *vs.* reaction pressure.

	R-OH	°C		R-OH	°C
⊖	CH_3-	100	◒	*n*-C_3H_7-	120
○	CH_3-	110	◓	*iso*-C_3H_7-	120
⦶	CH_3-	120	◐	*n*-C_4H_9-	120
⊗	C_2H_5-	120	◑	*s*-C_4H_9-	120

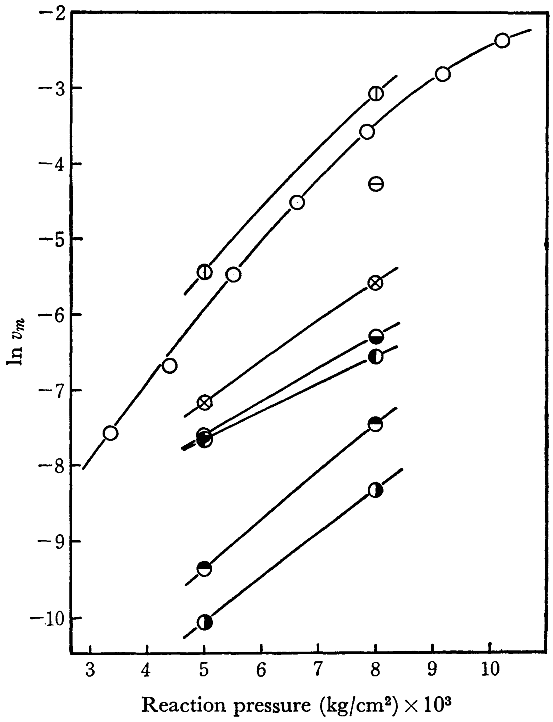


Fig. 4. Plots of the natural logarithm of v_m, which is the mean rate of the formation of TPT in Eq. (3), *vs.* reaction pressure.

	R-OH	°C		R-OH	°C
⊖	CH_3-	100	◒	*n*-C_3H_7-	120
○	CH_3-	110	◓	*iso*-C_3H_7-	120
⦶	CH_3-	120	◐	*n*-C_4H_9-	120
⊗	C_2H_5-	120	◑	*s*-C_4H_9-	120

the formation of TPT is a second-order reaction with respect to the IE concentration. It can be inferred from these results that TPT is formed through a relatively slow dimerization of IE, followed by the cyclization of the dimer with another molecule of IE. The reaction mechanism is given by:

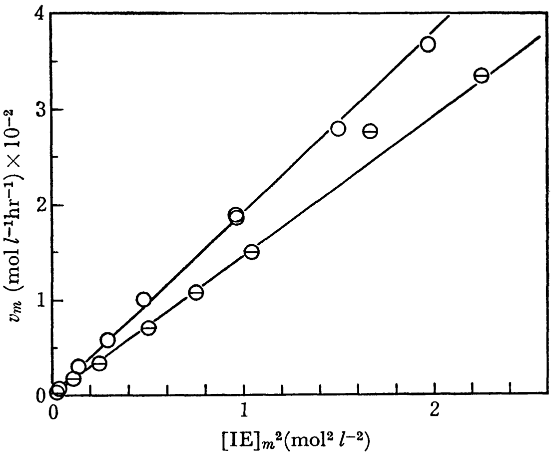


Fig. 5. Relation between the mean rate of the formation of TPT, v_m, and the mean concentration of MBI, $[IE]_m$, in the various initial ratio of C_6H_5CN:CH_3OH at 120°C.

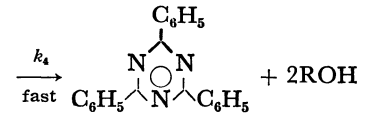
○, 7850 kg/cm²; ⊖, 6000 kg/cm²

The initial concentrations of MBI, $[IE]_i$, was calculated from the data in Table 1 and listed in the following table together with the observed concentrations of it, $[IE]_{obs}$, at ten hours after the initiation of the runs.

C_6H_5CN:CH_3OH (mol)	$[IE]_{obs}$ (mol/l)	$[IE]_i$ (mol/l)
7850 kg/cm²		
1:79.3	0.170	0.212
1:39.1	0.337	0.412
1:25.1	0.484	0.607
1:19.2	0.605	0.778
1:12.1	0.837	1.129
1:8.86	0.835	1.125
1:7.26	1.023	1.423
1:4.66	1.187	1.622
6000 kg/cm²		
C_6H_5CN:CH_3OH (mol)	$[IE]_{obs}$ (mol/l)	$[IE]_i$ (mol/l)
1:61.6	0.140	0.191
1:29.8	0.289	0.389
1:18.2	0.511	0.626
1:12.8	0.657	0.871
1:9.64	0.807	0.930
1:7.48	0.949	1.092
1:4.78	1.212	1.372
1:3.21	1.442	1.560

$$2C_6H_5C(NH)OR \xrightarrow[\text{slow}]{k_3} C_6H_5C(OR)\text{=}N\text{-}C(NH)C_6H_5 + ROH \quad (4)$$

$$C_6H_5C(OR)\text{=}N\text{-}C(NH)C_6H_5 + C_6H_5C(NH)OR$$



(5)

Here, we propose alkoxybenzimidoylbenzamidine[9] as the structure of the dimer.

If Eq. (4) is the rate-determining step in the formation of TPT, the rate of the formation of TPT is given as:

$$d[TPT]/dt = k_3[IE]^2, \quad (6)$$

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[9] Yakubovich had obtained a dimer of perfluoroadipo(or glutaro-)iminoether hydrochloride which has a similar structure.[10]

[10] A. Ya. Yakubovich, E. L. Zaitseva, R. M. Gitina, U. P. Bazov, I. M. Filatova, and G. I. Braz, *J. General Chem. U. S. S. R.*, **36**, 878 (1966).

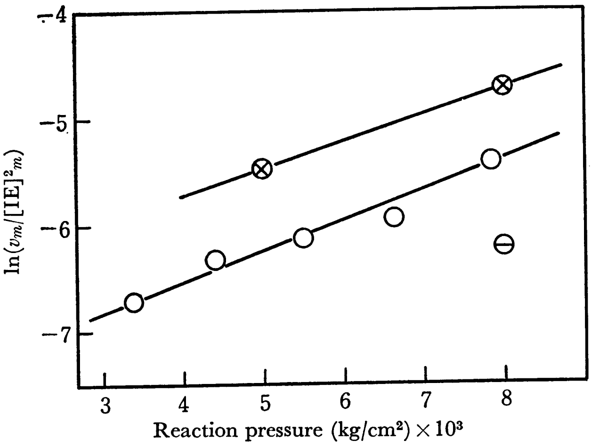

Fig. 6. Plots of $v_m/[IE]_m^2$, which is the rate of Eq. (4) expressed by Eq. (8), *vs.* reaction pressure at 100—120°C for 10 hr in the initial ratio of C_6H_5CN:CH_3OH=1: 3.2.
⊖, 100°C; ○, 110°C; ⊗, 120°C

where k_3 is the rate constant of Eq. (4). From Eq. (3), v_m can be expressed as:

$$v_m \approx d[TPT]/dt \quad (7)$$

and:

$$k_3 \approx v_m/[IE]_m^2 \quad (8)$$

By plotting the natural logarithm of $v_m/[IE]_m^2$ against the reaction pressure (Fig. 6), the activation volume (ΔV^{*}) of Eq. (4) was determined to be 9 m*l* mol^{-1} in the range of 3000—8000 kg/cm². This indicates that the effect of the pressure on this rate-determining step is relatively small. The marked effect of the pressure on the formation of TPT can, therefore, be mainly ascribed to the fact that pressure shifts the equilibrium of Eq. (1) toward the right.

Figure 7 shows that the value of v_m is at its maximum when the mixing ratio of benzonitrile to methanol is in the range of from 1: 3/2 to 1: 2/3 in weight or from 1: 3 to 1: 2 in molar ratio. The presences of these maxima are expected from Eqs (6) and (2), which mean that the rate of the formation of TPT is proportional to the square of the concentration of IE, *i.e.*, to those of the concentration of benzonitrile and methanol respectively; those facts are important for the effective use of the capacity of the pressure vessel.

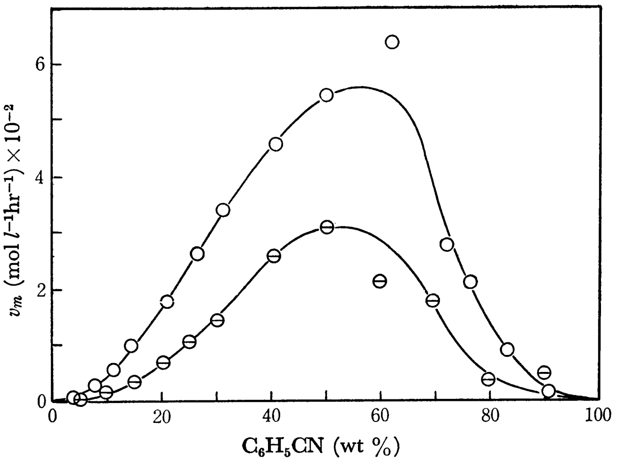

Fig. 7. Relation between the mean rate of the formation of TPT and the initial ratio of C_6H_5CN: CH_3OH at 120°C for 10 hr.
○, 7850 kg/cm² ⊖, 6000 kg/cm²

As is shown in Table 4, the addition of a small amount of acids stopped the formation of both MBI and TPT, while the addition of bases had little effect on their formation. These results obtained under high pressure differ from those of the commonly-employed synthetic methods, in which a large amount of strong

Table 4. Effect of acids and bases[a)]

Starting substances			Yields (%)		
C_6H_5CN: CH_3OH (wt ratio)	Reagents	(mol/ C_6H_5CN)	C_6H_5CN	MBI	TPT
1:1			50.2	50.0	3.63
1:0.5			66.1	24.8	2.09
1:1	Hydrogen chloride	0.1			0.0
1:1	Acetic acid	0.1	93.0	0.0	0.0
1:0.85	Pyridine	0.2	74.2	19.9	3.41
1:0.77	Triethylamine	0.2	82.9	6.91	1.03

a) Reaction conditions: 6600 kg/cm², 100°C, 10 hr.

Table 5. Effect of approtic solvents[a)]

Reactants (g)		Solvents				Yields (%)			Relative[b)] velocities
				Dielectric constants					
C_6H_5CN	CH_3OH	Substances	(g)	(ε_r)	(°C)	C_6H_5CN	MBI	TPT	
2.49	1.25	Dioxane	1.25	2.03	(25)	74.4	20.7	0.02	0.21
2.23	1.12	$(Et_2)O$	1.12	4.34	(20)	76.3	24.2	0.21	0.28
2.43	1.22	$(Me_2N)_3PO$	1.22	30	(20)	72.2	17.2	2.53	2.66
3.17	1.59			(33)[c)]	(25)	66.1	24.8	2.09	1.00
2.51	1.26	$C_6H_5NO_2$	1.26	34.8	(25)	69.6	25.5	1.35	1.28
2.52	1.26	$AcN(Me)_2$	1.26	37.7	(20)	59.5	23.8	11.1	12.4
2.50	0.0	$HC(O)N(Me)_2$	2.50	37.7	(20)	107.2	0.0	0.0	0.0
2.46	1.23	$HC(O)N(Me)_2$	1.23	37.7	(20)	64.0	13.3	18.1	18.4
2.51	1.25	AcNHMe	1.26	179	(30)	57.4	23.4	12.2	13.6

a) Reaction conditions: 6600 kg/cm², 100°C 10 hr.
b) $v_m/[IE]_m^2$ are recalculated by taking the value of the run, in which no solvent was added, as unity.
c) Dielectric constants of C_6H_5CN and CH_3OH are 25.2 and 33 respectively, at 25°C.

acids[11-13] or bases[14] are necessary for the direct formation of *s*-triazines from nitriles (having no α-hydrogen). Weakly acidic conditions are also required for the trimerization of IE.[2,10] When a part of the methanol in the initial mixture was replaced by some aprotic solvent, the $v_m/[\mathrm{IE}]_m^2$ ratio decreased in the decreasing order of the dielectric constant (see Table 5). These results suggest that the solvation of IE or its dimer, which is expected to be of a considerably polar nature, causes the rate of Eq. (4) to increase.

The procedure mentioned above may be a useful method of preparing various types of IE and trisubstituted-*s*-triazines, because it requires no chemically-reactive catalyst. For example, the three isomers of cyanopyridine were trimerized into the corresponding tripyridyl-*s*-triazines in an almost quantitative yield in the presence of methanol.

Experimental

Materials. Benzonitrile and the six alcohols, all of an EP grade, were carefully dried and distilled. Their water contents were determined by the Karl-Fisher method and were found to be less than 0.02%. The hydrochloride of IE was obtained by Pinner's method by introducing hydrogen chloride into a mixture of benzonitrile and alcohol. The resulting hydrochloride was neutralized, and the IE liberated was extracted and finally distilled. MBI: Yield, 74.5%; bp 61.5—62.3°C/3 mmHg; d_4^{20} 1.0684; n_D^{20} 1.5442; content, 98.7% by gas-liquid phase chromatography (glc). Ethylbenziminoether: 77.0%; 96.2—97.8°C/10 mmHg; 1.0312; 1.5295; 95.7%. *n*-Propyl-: 74.8%; 92°C/4 mmHg; 1.0392; 1.5220; 96.9%. Isopropyl-: 32.6%; 73°C/4 mmHg; 1.0274; 1.5171; 95.0%. *n*-Butyl-: 63.9%; 102—104°C/4 mmHg; 1.0241; 1.5179; 99.6%. *sec*-Butyl-: 21.5%; 86.6°C/2 mmHg; 1.0159; 1.5132; 98.7%. The impurities in IE thus prepared were mainly benzonitrile and/or benzoates. The cyanopyridines were supplied by Koei Chem. Ind., and the melting points of α-, β-, and γ- were 28.3°C, 38.7°C, and 78.6°C respectively.

Reaction Apparatus and Procedure. Collapsible lead capsules with a volume of a few milliliters were filled with the starting materials and put into a Bridgeman-type pressure vessel, in which less than twelve capsules could be placed, and compressed just below the desired pressure by introducing compressed oil from the pressure generator. Then the vessel was quickly heated for 30—40 min until the temperature inside its wall reached just below the desired level; thereafter, the pressure and the temperature were maintained at the desired levels. The reaction pressure was determined by means of a manganin-cell-type assembly corrected by the phase transition pressure of mercury. When the desired reaction time had passed, the temperature of the vessel was reduced to 50°C or less within 30—50 min in order to stop the reaction by cooling the wall with water. Sometimes a glass syringe or a polytetrafluoroethylene capsule was employed; no substantial wall effect was found.

Analysis. For the determination of benzonitrile and IE, glc (Reoplex 400, 4 mm i.d. × 750 mm, 50—250°C, 4°C/min) was employed. The TPT was filtered from the reaction medium, washed in methanol, recrystallized from toluene, and weighed. Solubility correction was made for the calculation of the yield of TPT.

Identification. MBI: A mixture of benzonitrile and methanol (each 2.2 g) was treated at 120°C and at 7800 kg/cm² for 5 hr and then fractionated by glc. The IR spectrum and the retention time of the glc of the fraction (0.5 g) at 150—160°C agreed with those of the authentic sample mentioned above (Found: C, 70.64; H, 6.66; N, 10.86%). The other five preparations of IE were identified by the retention time of glc with the respective authentic samples. TPT: 4.2-g portions of benzonitrile and methanol were similarly treated at 7800 kg/cm² and at 145°C for 3 hr, the product was diluted with methanol and filtered. The TPT (mp 236.8°C; yield, 3.34 g and 79.1%) thus separated was recrystallized from toluene as fine needles (Found: N, 14.14%; mp 237.1°C; mol wt (mass spectroscopy (MS)) 309). The IR spectrum and melting point agreed with those of the authentic sample prepared by the trimerization of benzonitrile in the presence of chlorosulfonic acid.[11] Tris(2-pyridyl)-*s*-triazine: 8.73-g portions of 2-cyanopyridine and methanol were treated at 100°C and at 8000 kg/cm² for 24 hr. The triazine thus produced was completely precipitated by the addition of water (yield, 8.62 g (98.6%)) and was recrystallized from water (Found: C, 69.14; H, 3.92; N, 27.08%; mp 256°C). The melting point and IR spectrum agreed with those of an authentic sample (Tokyo Chem. Ind.; mp 255°C). Tris(3-pyridyl)-: 9.37-g portions of nicotinonitrile and methanol were treated at 100°C and at 8000 kg/cm² for 30 hr. The precipitate was filtered, washed in methanol, weighed 9.08 g (99.1%), and recrystallized from pyridine. Found: C, 68.94; H, 3.92; N, 27.04%; mp 311°C; mol wt (MS), 312; IR, 1580, 1520, 1360 cm⁻¹ for the triazine ring. Calcd for $C_{18}H_{12}N_6$: C, 69.22; H, 3.87; N, 26.91%; mol wt, 312. Tris(4-pyridyl)-: 8.92-g portions of isonicotinonitrile and methanol were treated similarly; the product was filtered and washed in methanol to yield 6.71 g (75.2%). The crude triazine was recrystallized from pyridine. Found: C, 69.29; H, 4.01; N, 26.81%; mp 374°C; mol wt (MS), 312; IR, 1570, 1515, 1370 cm⁻¹. Calcd for $C_{18}H_{12}N_6$: C, 69.22; H, 3.87; N, 26.91%; mol wt, 312. A conciderable amount of an oily matter containing the triazine was also separated.

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