Synthesis of Succinonitrile by the Catalytic Reaction of Acrylonitrile in a Gaseous Phase

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During the course of an investigation of synthesizing adiponitrile by hydrodimerization of acrylonitrile in a gaseous phase, it has been found that succinonitrile is selectively produced from acrylonitrile by the catalytic reaction on a catalyst consisting of alkali and alkaline earth metal oxides. The conventional methods for the preparation of succinonitrile are based on, 1) the reaction between acrylonitrile and hydrogen cyanide in a liquid phase,[1] 2) the reaction between ethylene and hydrogen cyanide in a gaseous phase,[2] and 3) the irradiation of γ-rays onto acetonitrile molecule,[3] *etc.* The present work has an advantage in that succinonitrile can be prepared from acrylonitrile alone.

Acrylonitrile was made to react in a tubular flow reactor with fixed bed under the following conditions; fused silica tube 750×12 mm diam., catalyst 15 g (magnesium oxide: sodium oxide= 2 : 1 in moles, calcined at 500°C for 6 hr), reaction temp. 250—500°C, pressure 1 atm, W/F= 30—100 g-cat·hr/mol-feed, and hydrogen or nitrogen as a carrier gas. Gaseous components were trapped by ice-water, and analyzed by a gas chromatograph.

The liquid trapped weighed 90% of the acrylonitrile fed, and the succinonitrile content in the product was around 90 mol%. The results obtained are shown in Table 1 and Fig. 1. No acetylene was detected in the exhaust gas for 2 hr after initiation of the reaction, while it was confirmed in the sample prepared after 6 hr. This may be understood by taking the acetylide formation into consideration, that is, the reaction between alkali metal and acetylene. Hydrogen cyanide was more or less detected irrespective of the reaction time. It was further confirmed that acrylonitrile is not thermally decomposed if the reaction temperature is below 500°C and the catalyst is absent.

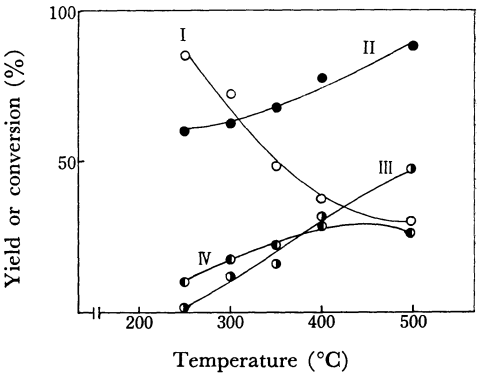

Fig. 1. Relationship between the yield or conversion and reaction temperature.
I: Succinonitrile, II: Conversion, III: Propionitrile, IV: Acetonitrile

From the results the reaction is supposed to proceed in accordance with the following in which acrylonitrile is decomposed into acetylene and hydrogen cyanide, followed by the Michael-type addition.

$$CH_2{=}CHCN \rightarrow CH{\equiv}CH + HCN \quad (1)$$

$$HCN + CH_2{=}CHCN \xrightarrow{\text{base catalyst}} NCCH_2CH_2CN \quad (2)$$

As seen in Fig.1, the yield of succinonitrile decreased with the rise of temperature while the yields of propionitrile and acetonitrile increased. In general, succinonitrile is synthesized favorably at 250°C or below.

TABLE 1.

Feed of Hydrogen (ml/min)	Feed of AN (g/hr)	Liquid trapped/hr					Untrapped products (g/hr)
		Weight (g)	AN obtained (mol)	SN obtained (mol)	AcN obtained (mol)	PN obtained (mol)	
100	0.88	0.75	0.32×10^{-2}	0.70×10^{-2}	0.04×10^{-2}	0.01×10^{-2}	0.13
150	1.16	1.08	1.45×10^{-2}	0.37×10^{-2}	0.02×10^{-2}	0.02×10^{-2}	0.08
200	1.87	1.81	2.92×10^{-2}	0.25×10^{-2}	0.04×10^{-2}	0.04×10^{-2}	0.06
300	2.43	2.38	3.90×10^{-2}	0.22×10^{-2}	0.16×10^{-2}	0.10×10^{-2}	0.05

AN: Acrylonitrile, SN: Succinonitrile, AcN: Acetonitrile, PN: Propionitrile
The reaction was carried out under the following conditions: reaction temperature 250°C, catalyst 15 g (MgO: Na_2O=2 : 1 in mol), and pressure 1 atm.

1) P. L. Heider and H. M. Walker, U. S. 2698337 (1954).
2) C. R. Harris, U. S. 2427601 (1948).
3) D. Bradley and J. Wilkinson, *J. Chem. Soc.*, *A*, **1967** 531.