BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 396—401 (1968)

Dimerization of Acrylonitrile by Ruthenium Chloride

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(Received July 17, 1967)

The end-to-end dimerization of acrylonitrile was effected with a ruthenium trichloride trihydrate catalyst under a hydrogen atmosphere, thus obtaining a mixture of *cis*- and *trans*-1, 4-dicyano-1-butene as the main products. Under nitrogen, however, only very small amounts of these products were formed. The reaction occurred at temperatures of 120—200°C under moderate hydrogen pressures in alcoholic media such as ethanol. The effects of various salts or electron-donating compounds on the catalysis were examined.

Previously we reported[1] that acrylonitrile was, though not catalytically, converted at an elevated temperature to a mixture of propionitrile, 2-methylglutaronitrile, and adiponitrile with several systems involving hydride complexes of cobalt or iron. The end-to-end dimerization of methyl acrylate by a rhodium or ruthenium chloride catalyst has been found by Alderson *et al.*[2] However, acrylonitrile does not dimerize successfully in the same reaction. In this paper, we wish to report the successful catalytic dimerization of acrylonitrile, which primarily gives end-to-end coupling products. The reaction was effected with ruthenium trichloride trihydrate under a hydrogen atmosphere; it was not, however, catalytic under a nitrogen atmosphere. The variation in the reaction temperature and the hydrogen pressure was examined, and the effects of the addition of various salts or electron-donating compounds were also studied.

Results and Discussion

The reaction of acrylonitrile by the use of various second- and third-row transition metal compounds, especially chlorides, was investigated in order to obtain the dimers of acrylonitrile. A part of the results are shown in Table 1. The reaction of acrylonitrile by ruthenium chloride under a nitrogen atmosphere yielded only a small percentage of propionitrile and acrylonitrile dimers. The replacement of the nitrogen atmosphere with ethylene improved the yield of the dimers to 10%. When acrylonitrile was treated with an ethanol solution of ruthenium chloride under a hydrogen atmosphere, acrylonitrile was catalytically converted to a mixture of propionitrile and acrylonitrile dimers. Gas chromatographic analysis showed that the dimers were a mixture of three components. The three components were isolated by the fractional distillation of the mixture. The fraction with a bp of 107°C/2 mmHg was identified as adiponitrile by a comparison of the retention time and the infrared spectrum with those of an authentic sample. Both the fraction with a bp of 95°C/2 mmHg, A, and the fraction with a bp of 175—180°C/2 mmHg, B, were hydrogenated over palladium black at room temperature to

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[1] A. Misono, Y. Uchida, K. Tamai and M. Hidai, This Bulletin, **40**, 931 (1967).

[2] T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1965).

TABLE 1. THE REACTION OF ACRYLONITRILE IN THE PRESENCE OF TRANSITION METAL CHLORIDES[a]

Chlorides	mmoles	Reaction atmosphere	Reaction temp., °C	Reaction time, hr	Conv. %	PN[b] %, yield[c]	Dimers %, yield[c]
$RuCl_3 \cdot 3H_2O$	0.77	N_2, 1 atm	170	4	33	2	5
$RuCl_3 \cdot 3H_2O$	0.77	C_2H_4, 10 atm	170	5	15	3	10
$RuCl_3 \cdot 3H_2O$	0.77	H_2, 30 atm	150	0.5	94	51	44
$RhCl_3 \cdot 3H_2O$	0.76	H_2, 30 atm	140	1.3	60	60	
$MoCl_5$	2.2	H_2, 30 atm	120	3	18	11	
$MoCl_5$	1.3	H_2, 30 atm	170	3	85	15	
WCl_6	1.8	H_2, 30 atm	120	3	10	7	
$IrCl_4$	0.59	H_2, 30 atm	170	3	55	45	
$PdCl_2$	0.77	H_2, 30 atm	140	0.5	79	74	

a) All reactions used 10m*l* of acrylonitrile and 20 m*l* of ethanol or methanol. b) Propionitrile.
c) % based on the acrylonitrile originally fed in.

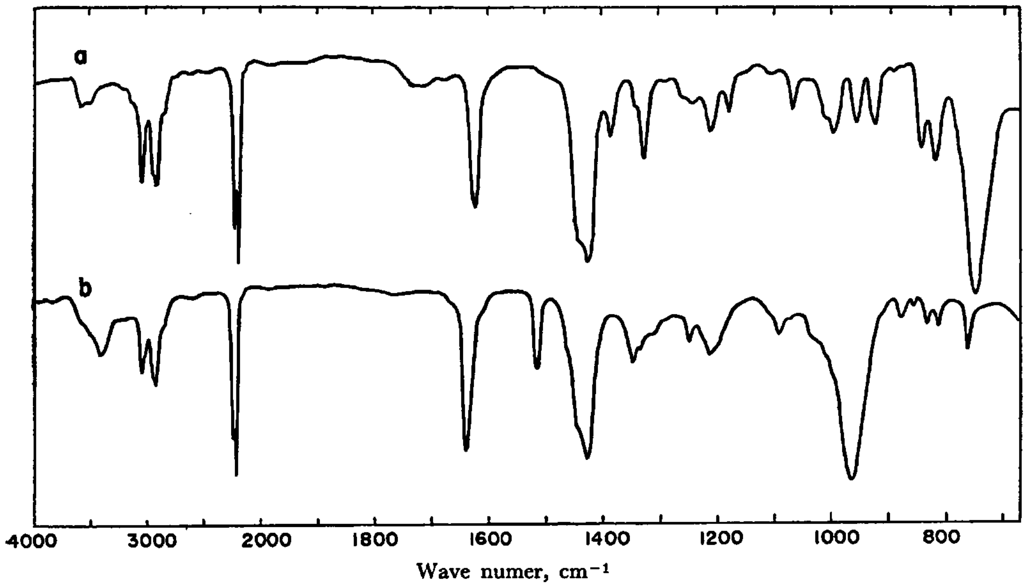
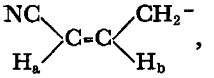
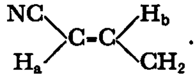


Fig. 1. Infrared spectra of (a) *cis*-1,4-dicyano-1-butene and (b) *trans*-1,4-dicyano-1-butene.

give adiponitrile. The amount of hydrogen gas absorbed indicated that both A and B were dimers of acrylonitrile carrying a double bond. The infrared spectrum of A (Fig. 1) showed the presence of two different nitrile groups (*ca.* 2230 and 2210 cm^{-1}) and a cis double bond (1630 and 750 cm^{-1}). The NMR spectrum of A (Fig. 2) showed the complex bands at $\tau=7.9$, a doublet at $\tau=4.9$, and the complex band at $\tau=4.1$ in an intensity ratio of 4 : 1 : 1. The bands at $\tau=7.9$ were assignable to the four methylene protons of $-CH_2CN$ and $-CH_2-CH{=}CH-$. The doublet at $\tau=4.9$ with a spin-spin coupling constant of 10 cps was assigned to the cis olefinic proton, H_a, in


$\mathrm{(NC)(H_a)C{=}C(CH_2{-})(H_b)}$

, while the band at $\tau=4.1$ was assigned to the other olefinic proton, H_b. On the other hand, the infrared spectrum of B (Fig. 1) showed the presence of two different nitrile groups (*ca.* 2240 and 2220 cm^{-1}) and a trans double bond (1640 and 965 cm^{-1}). The NMR spectrum of B (Fig. 2) showed a doublet at $\tau=5.1$ with a large spin-spin coupling constant of 16 cps; it was assigned to the trans olefinic proton, H_a, in


$\mathrm{(NC)(H_a)C{=}C(H_b)(CH_2)}$

. From these results, A and B were identified as *cis*- and *trans*-1, 4-dicyano-1-butene respectively.

$$CH_2{=}CHCN \xrightarrow[\text{under } H_2]{RuCl_3 \cdot 3H_2O} \left\{\begin{array}{l} CH_3CH_2CN \\ NCCH{=}CHCH_2CH_2CN \text{ (cis and trans)} \\ NC(CH_2)_4CN \end{array}\right.$$

Other transition metal chlorides, such as rhodium, palladium, tungsten, molybdenum, or iridium chlorides, gave only propionitrile in reactions

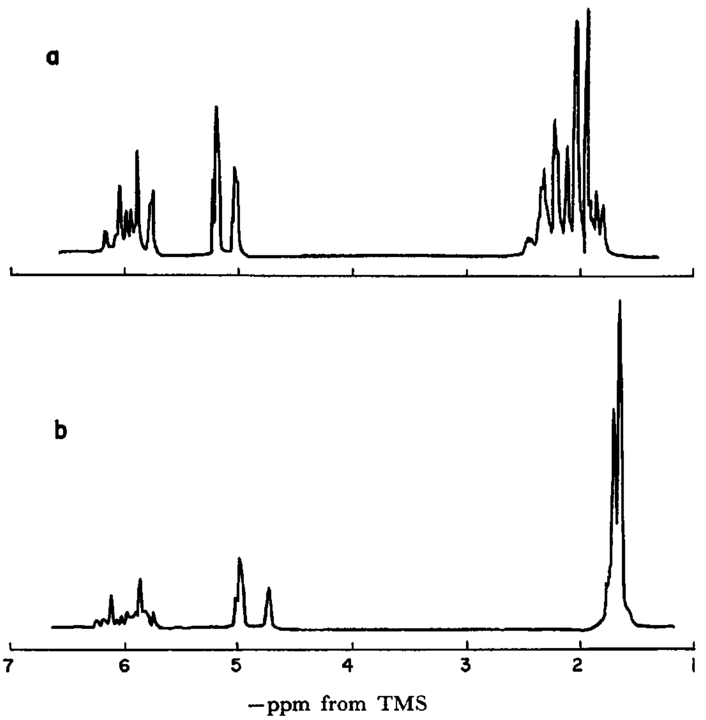


Fig. 2. NMR spectra of (a) *cis*-1, 4-dicyano-1-butene and (b) *trans*-1, 4-dicyano-1-butene in benzene.

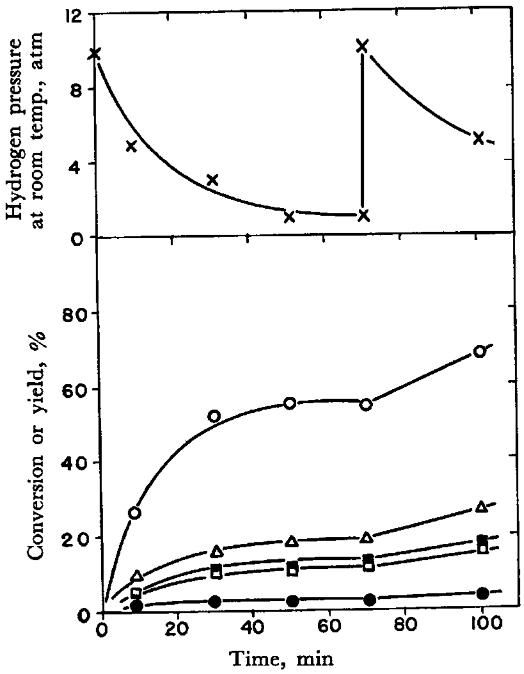


Fig. 3. Relationship between reaction time and hydrogen pressure or yields of products at 150°C: ○, conversion of acrylonitrile; △, yield of propionitrile; □, yield of *cis*-1, 4-dicyano-1-butene; ●, yield of adiponitrile; ■, yield of *trans*-1, 4-dicyano-1-butene.

under a hydrogen atmosphere.

In this catalytic conversion of acrylonitrile to a mixture of *cis*- and *trans*-1, 4-dicyano-1-butene, adiponitrile, and propionitrile by the use of ruthenium chloride, hydrogen appears to play an important role in the reaction mechanism, as the reaction did not proceed catalytically in the absence of hydrogen. Figure 3 shows the relationship between the reaction time or the hydrogen pressure and the yields of the products. When 10 atm of hydrogen (the pressure at room temperature) was charged into the reaction vessel at 150°C, a rapid uptake of hydrogen occurred, and propionitrile and the dimers were formed. When the hydrogen pressure (converted to the value at room temperature) went below 1 or 2 atm after *ca.* 30 min, the reaction of acrylonitrile nearly stopped. However, when another 9 atm of hydrogen was charged into the reaction vessel after 70 min, the absorption of hydrogen again started, and propionitrile and the dimers were obtained. This would suggest that the reaction proceeds through a ruthenium hydride complex, which is regenerated by a large amount of hydrogen. We have already reported(3) that two yellow complexes, which catalyzed the dimerization of acrylonitrile, were obtained by the reaction of acrylonitrile and ruthenium trichloride under a nitrogen or hydrogen

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3) A. Misono, Y. Uchida, M. Hidai and H. Kanai, *Chem. Commun.*, 357 (1967).

atmosphere. The first complex, $(CH_2{=}CHCN)_3RuCl_2$, was obtained by refluxing a solution of ruthenium trichloride in ethanol with a large excess of acrylonitrile under nitrogen. In the complex, acrylonitrile was bonded to the metal through the nitrogen lone pair. The other complex obtained by the reaction under hydrogen at 150°C had a cyanoethyl group attached to the metal. The following reaction mechanism may be assumed on the basis of these results. An intermediate complex may be formed in the reaction in which a hydride ion and at least two molecules of acrylonitrile are coordinated to ruthenium. When a cyanoethyl group formed by the insertion reaction of acrylonitrile into the ruthenium-hydride bond reacts with hydrogen, propionitrile will be formed, while a dicyanobutyl complex will be formed by the insertion of an acrylonitrile molecule into the ruthenium-cyanoethyl bond. This dicyanobutyl complex may decompose to give 1,4-dicyano-1-butene or may react with hydrogen to yield adiponitrile.

Figure 4 shows the effect of the initial hydrogen pressure on the reaction. The yields of propionitrile and adiponitrile increased with an increase in the initial hydrogen pressure, while the yield of 1,4-dicyano-1-butene decreased. This would imply that, under a high hydrogen pressure, a cyanoethyl complex and a dicyanobutyl complex easily react with hydrogen to give propionitrile and adiponitrile respectively.

The formation of the dimers and propionitrile is strongly dependent on the reaction temperature, as Fig. 5 shows. Below 120°C, the reaction was slow. The conversion of acrylonitrile varied with the reaction temperature, although the composition of the products was almost unchanged at temperatures of 140—180°C. Above *ca.* 180°C, the yield of propionitrile gradually decreased, while the yield of the dimers greatly decreased with an increase in the reaction temperature. These may be explained by the thermal instability of such reaction intermediates as a hydride complex and a cyanoethyl complex.

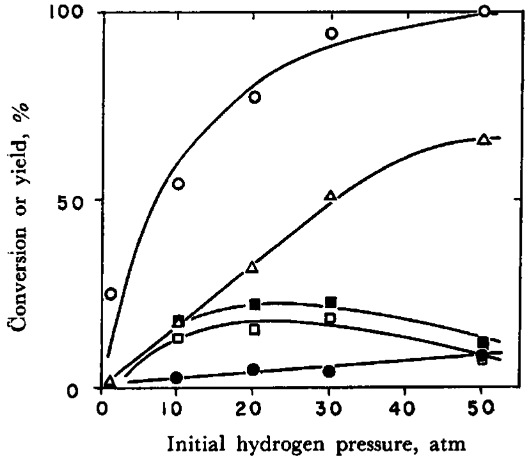

Fig. 4. The effect of initial hydrogen pressure on the formation of products: reaction temp., 150°C; about 0.5 hr was used for heating up, and the mixture was kept at 150°C for 0.5 hr; ○, conversion of acrylonitrile; △, yield of propionitrile; □, yield of *cis*-1,4-dicyano-1-butene; ●, yield of adiponitrile; ■, yield of *trans*-1,4-dicyano-1-butene.

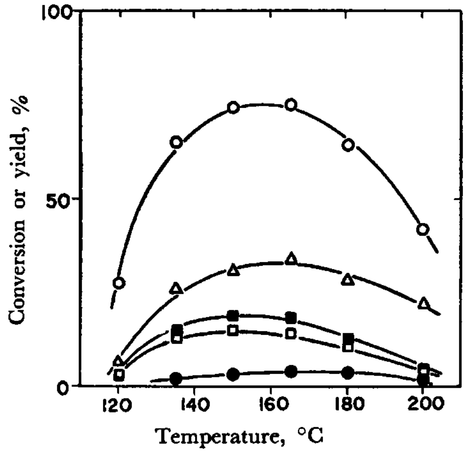

Fig. 5. The effect of reaction temperature on the formation of products: initial hydrogen pressure, 20 atm; reaction time, 40 min; ○, conversion of acrylonitrile; △, yield of propionitrile; □, yield of *cis*-1,4-dicyano-1-butene; ●, yield of adiponitrile; ■, yield of *trans*-1,4-dicyano-1-butene.

Various salts or electron-donating compounds were added to the reaction solution in order to change the valency state of ruthenium or to replace the ligands of ruthenium trichloride with other ligands. The results of the addition of those compounds are given in Table 2. Propionitrile was mainly formed when acrylonitrile was treated under a hydrogen atmosphere with a dark-blue ethanol solution of ruthenium(II) chloride prepared by the reduction of ruthenium trichloride with titanium trichloride. This ruthenium(II) chloride has been known to catalyze the homogeneous hydrogenation of olefinic bonds in compounds, such as maleic, fumaric, and acrylic acids, in which the double bond is activated by the presence of an adjacent carboxyl group.[4] Wilkinson has reported[5] that, on heating solutions of ruthenium trichloride trihydrate with tin dichloride in ethanol, dark-blue solutions which appear to contain ruthenium(II) are obtained. The addition of tin dichloride to the reaction solution also gave propionitrile as the main product.

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4) J. Halpern, J. F. Harrod and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961); *ibid.*, **88**, 5150 (1966).

5) J. F. Young, R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1964**, 5176.

TABLE 2. EFFECTS OF ADDITIVES ON THE FORMATION OF PRODUCTS[a]

Additives	Add./Ru[b]	Reaction temp., °C	Conv. %	PN	ADN	cis	trans[c]
					%, yield		
none		150	94	51	4	18	22
none		170	94	54	6	13	17
$TiCl_3$	10	170	72	43	t[d]	t	t
$SnCl_2 \cdot 2H_2O$	5	170	42	26	1	2	2
LiCl	10	170	100	54	9	16	21
KCl	5	170	98	53	6	14	14
LiBr	6	150	93	49	4	15	20
NaI	2	150	91	39	5	15	18
C_5H_5N	1	150	65	32	2	12	16
C_5H_5N	2	150	10	6		t	t
	11	170	92	52	6	16	24

a) Reaction conditions: 10m*l* of acrylonitrile; 20m*l* of ethanol; 0.200 g of $RuCl_3 \cdot 3H_2O$; 30 atm of initial hydrogen pressure. About 0.5 hr was used for heating up, and the mixture was kept at the designated temperature for 0.5 hr. b) Molar ratio of an additive to $RuCl_3 \cdot 3H_2O$. c) Abbreviations: PN, propionitrile; ADN, adiponitrile; cis, *cis*-1, 4-dicyano-1-butene; trans, *trans*-1, 4-dicyano-1-butene. d) Trace.

On the other hand, the reaction was hardly affected at all when potassium chloride, lithium chloride, lithium bromide, or sodium iodide was added to the reaction solution in order to vary the concentration of chloride ions or in order to replace the chloride ions of ruthenium trichloride with bromide or iodide ions.[6] The reaction was, however, strongly inhibited by the addition of two moles of pyridine per mole of ruthenium trichloride to the reaction solution. This may be explained by the coordination of pyridine to ruthenium, which prevents the coordination of the acrylonitrile molecules or the activation of the hydrogen molecule. The reaction was, however, hardly affected at all by the addition of large amounts of quinoline, which is a weaker coordinating agent than pyridine. In the dimerization of acrylonitrile, three coordination sites around the ruthenium atom may be required for a hydride ion and two molecules of acrylonitrile, as in the case of the dimerization of ethylene using a rhodium trichloride catalyst.[7] The reaction may be strongly affected when other ligands such as pyridine occupy those coordination sites.

Experimental

Reagents. Acrylonitrile was distilled under nitrogen, and 0.1% of hydroquinone was added to the acrylonitrile distilled. Methanol and ethanol were dried with Drierite and distilled under nitrogen. All transition-metal chlorides were commercially obtained.

The Reaction of Acrylonitrile by the Use of Ruthenium Trichloride Trihydrate. *A. The Reaction under a Nitrogen Atmosphere.* A 100-m*l* stainless-steel autoclave was charged with 20 m*l* of ethanol, 10 m*l* of acrylonitrile, and 0.200 g of ruthenium trichloride trihydrate under nitrogen. The mixture was then heated to 170°C and kept at that temperature for 4 hr. The reaction products, when quantitatively analyzed by means of gas chromatography, were found to be propionitrile (2% of the acrylonitrile originally fed in) and *cis*- and *trans*-1, 4-dicyano-1-butene (5%).

B. The Reaction under a Hydrogen Atmosphere. A reaction solution was prepared as above. The atmosphere was replaced with 30 atm of hydrogen, and the mixture was heated to 150°C. About 0.5 hr was used for the heating-up, after which the mixture was kept at 150°C for 0.5 hr. Gas chromatographic analysis showed that the products were propionitrile (51%), adiponitrile (4%), *cis*-1, 4-dicyano-1-butene (18%), and *trans*-1, 4-dicyano-1-butene (22%). The conversion of acrylonitrile was 94%.

In order to examine the effects of the reaction temperature and the reaction time on the formation of the products, the reaction mixture prepared under a nitrogen atmosphere was heated up to a reaction temperature, and hydrogen gas of a definite pressure was charged into the reactor at that temperature. A rapid uptake of hydrogen occurred, and propionitrile, *cis*- and *trans*-1, 4-dicyano-1-butene, and adiponitrile were formed.

C. Addition of Salts or Electron-donating Compounds. A reaction solution was prepared as above except that a calculated amount of an additive was added. The atmosphere was replaced with 30 atm of hydrogen, and then the mixture was heated to 150 or 170°C and kept at that temperature for 0.5 hr. The products were analyzed by gas chromatography.

The Reaction of Acrylonitrile by the Use of Other Transition-metal Chlorides. The reaction solution was prepared in a way similar to that used in the case of ruthenium chloride. The atmosphere was

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6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York (1962), p. 818; T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

7) R. Cramer, *J. Am. Chem. Soc.*, **87**, 4717 (1965).

replaced with 30 atm of hydrogen, and the mixture was heated to a reaction temperature. The products were analyzed by gas chromatography.

Isolation and Identification of the Products. The reaction products were isolated by the fractional distillation of the reaction solution. Propionitrile and adiponitrile were identified by a comparison of their retention times and infrared spectra with those of authentic samples. The *cis*- and *trans*-1, 4-dicyano-1-butene isolated by the fractional distillation were characterized by their infrared and NMR spectra. They were hydrogenated over palladium black at room temperature to give adiponitrile.

Gas Chromatographic Analysis of the Products. For the analysis of acrylonitrile and propionitrile, a 2.5-m tricresyl phosphate column was used. The conditions were: column temperature, 100°C; flash evaporator temperature, 150°C; helium gas speed, 40 m*l*/min. For the analysis of *cis*- and *trans*-1, 4-dicyano-1-butene and adiponitrile, a 2-m polyoxyethylene sorbitan monooleate column was used, and the conditions were: column temperature, 200°C; inlet temperature, 250°C; helium gas speed, 50 m*l*/min.