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The Hydrodimerization of Acrylonitrile*[1]

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During the course of our studies of the dimerization of such vinyl monomers as acrylonitrile or acrolein with various Ziegler-type catalysts or metal carbonyls, it has been found that acrylonitrile is converted at an elevated temperature in an iron or cobalt carbonyl - alkali - water system, an iron or cobalt carbonyl - sodium borohydride or -lithium aluminum hydride system, or a cobalt carbonyl - H_2 system to hydrodimers of acrylonitrile composed of adiponitrile and 2-methylglutaronitrile as well as propionitrile. Some iron carbonyl hydrides, which are presumably formed as intermediates in these reactions, were therefore prepared and subjected to reaction with acrylonitrile, 3-chloropropionitrile, or ethyl acrylate. On the basis of these experimental results, a reaction mechanism containing a cyanoethyl complex as an intermediate was proposed for the formation of hydrodimers of acrylonitrile.

Although many catalyst systems composed of a transition metal compound and an organometallic compound have been found for the oligomerization of diene monomers or for the cooligomerization of diene monomers and vinyl monomers, few catalysts for the oligomerization of vinyl monomers have been found; acrylic or methacrylic acid, methyl acrylate, and acrylonitrile or ethyl acrylate have, however, been reported to form dimers in the presence of pentacyanocobaltate(II),¹⁾ rhodium or ruthenium chloride,²⁾ and tertiary phosphine³⁾ catalysts respectively.

During the course of our studies of the dimerization of vinyl monomers with various Ziegler-type catalysts or metal carbonyls, it has been found that when acrylonitrile is treated at an elevated temperature with an iron or cobalt carbonyl-alkali-water system, an iron or cobalt

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1) J. Kwiatek, I. L. Mador and J. K. Seyler, *Advan. Chem. Ser.*, **37**, 201 (1963).

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

3) P. Chabardes, C. Grard and M. Thiers, Fr. Pat. 1366081 (1964); M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965); J. D. McClure, U. S. Pat. 3225083 (1965); M. Rauhut and H. Currier, U. S. Pat. 3074999 (1963).

carbonyl-sodium borohydride or -lithium aluminum hydride system, or a cobalt carbonyl-H_2 system, hydrodimers of acrylonitrile composed of adiponitrile and 2-methylglutaronitrile are yielded in addition to propionitrile.[4] Some iron carbonyl hydrides, which are presumably formed as intermediates in these reactions, were therefore prepared and subjected to reaction with acrylonitrile, 3-chloropropionitrile, or ethyl acrylate. On the basis of these experimental results, a reaction mechanism containing a cyanoethyl complex as an intermediate will be proposed for the formation of hydrodimers of acrylonitrile.

Results and Discussion

Hydrodimerization of Acrylonitrile. It is well known that the coordination of diene monomers to a transition metal atom plays an important role in the dimerization or trimerization of diene monomer by a transition metal complex catalyst. Therefore, in order to obtain dimers or codimers of acrylonitrile and acrolein, various catalyst systems in which a metal atom is presumably coordinated with those monomers were investigated; those monomers were treated with systems composed of various first-row transition metal acetylacetonate, triethylaluminum, and an electron donor compound, but no dimers were obtained. The reaction of those monomers with metal carbonyls, especially iron pentacarbonyl, was also studied since some complexes coordinated with those monomers have been prepared from metal carbonyls.[5] Although no dimers were formed in the reaction of acrylonitrile with iron carbonyl alone, the hydrodimers, not the dimers, were obtained when a combined system of iron pentacarbonyl, alkali, and water was used. Moreover, two other systems which also yielded the hydrodimers were found. The three systems are, then:

(I) Fe(Co)$_5$ or $Co_2(CO)_8$-Alkali-H_2O system

(II) Fe(Co)$_5$ or $Co_2(CO)_8$-$NaBH_4$ or $LiAlH_4$ system

(III) $Co_2(CO)_8$-H_2 system

The results of treatment of acrylonitrile with the above three systems are shown in Table 1. In the case of the system I, acrylonitrile reacted with water present in the system to form ethylene cyanohydrin and 2, 2′-dicyanoethylether besides propionitrile, 2-methylglutaronitrile, and adiponitrile. When an alkali methanol solution was used instead of an alkali aqueous solution, those compounds were not observed. The reaction under a hydrogen atmosphere greatly increased the yield of propionitrile, but the yields of hydrodimers were very similar to those in the reaction under a nitrogen atmosphere.

The system II also yielded propionitrile and hydrodimers, in which a branched hydrodimer, 2-methylglutaronitrile, was the main product.

When acrylonitrile was treated with dicobalt octacarbonyl under a nitrogen atmosphere, no dimers were observed, but treatment under a hydrogen atmosphere produced hydrodimers, especially the branched one (the system III).

Treatment of Acrylonitrile with the $Fe(CO)_5$-$NaOH$-H_2O System. As has been described above, the variation of the reaction atmosphere from nitrogen to hydrogen led to a large increase in the yield of propionitrile, but it did not change the yield of hydrodimers. This indicates that although the hydrogen required for the formation of propionitrile can be supplied from the reaction atmosphere, the hydrogen used for the formation of hydrodimers can be supplied only with

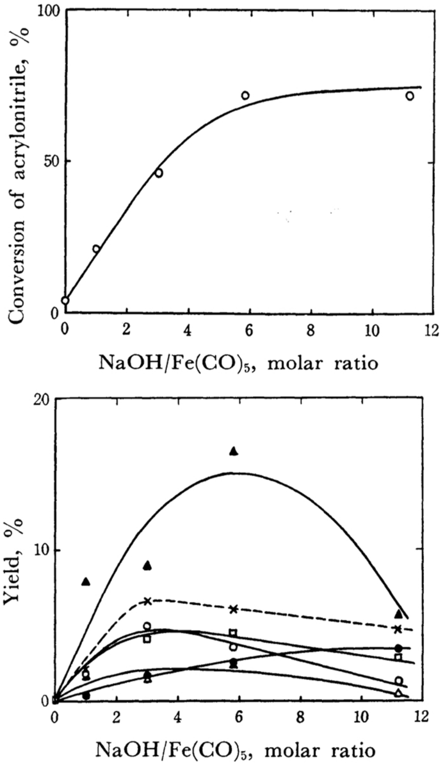

Fig. 1. The effects of molar ratio of NaOH to $Fe(CO)_5$.

□: PN, △: ECH, ●: GN, ○: ADN

▲: DCEE, ----: GN+ADN

Reaction conditions: 300 mmol of acrylonitrile; 20 *ml* of benzene; 10 mmol of $Fe(CO)_5$; 110°C; 4 hr under nitrogen

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[4] Recently similar systems to produce hydrodimers of acrylonitrile have been proposed as patents by Chabardes (Fr. 1381511 (1964), Fr. 1377425 (1964) and Fr. Addn. 85717 (1965)) and by Schreyer (U. S. 3206498 (1965)).

[5] G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); G. N. Schrauzer, *ibid.*, **82**, 1008 (1960); E. Weiss, K. Stark, J. E. Lancaster and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

TABLE 1. THE HYDRODIMERIZATION OF ACRYLONITRILE

No.	System, mmol	Reaction condition			Conversion %	Product				
		Atmosphere	Temp. °C	Time hr		PN	ECH	GN mmol	ADN	DCEE
1	$Fe(CO)_5$: 11, NaOH : 32, H_2O : 140	N_2	110	4	46	12	4.4	2.5	7.3	13
2	$Fe(CO)_5$: 11, NaOH : 31, H_2O : 140	H_2	110	4	55	50	4.4	4.6	6.8	9.8
3	$Fe(CO)_5$: 11, NaOH : 30, H_2O : 140	H_2	110	6.6	79	91	3.3	6.5	7.4	6.8
4	$Fe(CO)_5$: 11, NaOH : 30, H_2O : 130	H_2	150	4	88	140	t	9.5	5.2	
5*	$Fe(CO)_5$: 23, NaOH : 35	H_2	110	7	100	71		5.5	6.3	
6	$Fe(CO)_5$: 24, Na_2CO_3 : 33, H_2O : 140	H_2	110	7	54	97	8.9	4.0	9.5	4.4
7	$Fe(CO)_5$: 27, $Ba(OH)_2 \cdot 8H_2O$: 33	H_2	110	7	64	55	3.9	3.1	4.1	3.5
8	$Fe(CO)_5$: 22, NEt_3 : 35	H_2	110	7	38	31		1.3	3.2	
9	$Co_2(CO)_8$: 8.2, NaOH : 35, H_2O : 180	N_2	110	4	42	t	11	1.0		16
10	$Fe(CO)_5$: 9.7, $NaBH_4$: 29	N_2	110	5	40	11		1.2	t	
11	$Fe(CO)_5$: 8.3, $NaBH_4$: 26	H_2	110	7	45	62		4.5	3.5	
12	$Co_2(CO)_8$: 9.1, $LiAlH_4$: 26	H_2	110	5	69	11		1.2	t	
13	$Co_2(CO)_8$: 8.8, $NaBH_4$: 26	H_2	110	6	67	14		1.9	t	
14	$Co_2(CO)_8$: 11	H_2	110	7	45	15		1.7		

Abbreviations: PN: propionitrile, ECH: ethylene cyanohydrin, ADN: adiponitrile
GN: 2-methylglutaronitrile, DCEE: 2, 2'-dicyanoethyl ether

In each experiment, 300 mmol of acrylonitrile, 20 m*l* of benzene, and 0.3 g of hydroquinone as an polymerization inhibitor were employed and the pressure of the reaction atmosphere was 80 atm at −5°C.

* In this case, methanol was used instead of benzene.

difficulty from the hydrogen atmosphere; it is probably supplied from the OH^- or H_2O.

The effects of the molar ratio of NaOH to $Fe(CO)_5$ on the reaction are shown in Fig. 1. The yield of hydrodimers composed of adiponitrile and 2-methylglutaronitrile reached a maximum at a ratio of about 3. When the molar ratio became more than 3, the yield gradually decreased with the increase in the molar ratio. The composition of hydrodimers also varied with the molar ratio; at a molar ratio of about 11, the branched hydrodimer was mainly obtained.

Krumholz and Stettiner[6] have shown that the solutions obtained by treating iron pentacarbonyl with aqueous alkali contain the $[HFe(CO_4)]^-$ and/or $[Fe(CO)_4]^{2-}$ ions, depending on the amount of alkali used. When 1 mol of $Fe(CO)_5$ is treated with 3 moles of NaOH, the $[HFe(CO)_4]^-$ anion is formed according to Eq. (1):

$$Fe(CO)_5 + 3NaOH = NaHFe(CO)_4 + Na_2CO_3 + H_2O \qquad (1)$$

Treatment with 4 or more mol of NaOH produces the $[Fe(CO)_4]^{2-}$ anion according to Eq. (2):

$$Fe(CO)_5 + 4NaOH = Na_2Fe(CO)_4 + Na_2CO_3 + 2H_2O \qquad (2)$$

Since the dibasic salt $Na_2Fe(CO)_4$ is hydrolyzed to some extent according to Eq. (3), the $[HFe(CO)_4]^-$ ion is present even in a strongly alkaline solution.

$$Na_2Fe(CO)_4 + H_2O = NaOH + NaHFe(CO)_4 \qquad (3)$$

From a consideration of the above reaction of $Fe(CO)_5$ with aqueous alkali, it seems most reasonable to suppose that a hydride complex such as $[HFe(CO)_4]^-$ plays an important role in the formation of hydrodimers. Thus, the yield of hydrodimers reaches a maximum at the molar ratio of NaOH to $Fe(CO)_5$ of 3, which is the molar ratio required for the formation of the hydride complex, $NaHFe(CO)_4$, according to Eq. (1). When the molar ratio becomes more than 3, the yield decreases with decrease in the concentration of the hydride complex. Sternberg[7] has shown that a dark-red pyrophoric powder, a polynuclear hydride complex, is obtained by the reaction of $Fe(CO)_5$ and NaOH in a molar ratio of 1 : 3. When acrylonitrile was treated with the above complex under nitrogen, propionitrile and the hydrodimers were formed. This also supports the above view.

The Reaction of Acrylonitrile with Iron Carbonyl Hydride Complexes. It may be supposed that all three systems which yield the hydrodimers form a hydride complex as an intermediate, and that the hydride complex plays an important role in the formation of the hydrodimers, as has been described above. Some salts of mono or polynuclear iron carbonyl hydrides obtained by

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6) P. Krumholz and H. M. A. Stettiner, *J. Am. Chem. Soc.*, **71**, 3035 (1949).

7) H. W. Sternberg, R. Markby and I. Wender, *ibid.*, **79**, 6116 (1957).

TABLE 2. THE REACTION OF ACRYLONITRILE WITH SALTS OF IRON CARBONYL HYDRIDES

Hydride, mmol	CH_3OH m*l*	AN mmol	Conv. %	Product, mmol PN	GN	ADN
$[Ni(o\text{-phen})_3][HFe(CO)_4]_2$: 2.0	6	46	42	3.4	0.6	
$[Fe(o\text{-phen})_3][HFe(CO)_4]_2$: 0.38	2	15	53	0.3	t	
$[Ni(o\text{-phen})_3][HFe_2(CO)_8]_2$: 0.56	2	16	43	1.0		0.2
$[NEt_3H][HFe_3(CO)_{11}]$: 2.1	6	44	25	1.4		1.3

Reaction conditions: 50°C; 24 hr

TABLE 3. THE REACTION OF ACRYLONITRILE AND/OR 3-CHLOROPROPIONITRILE WITH THE HYDRIDE $[NEt_3H][HFe_3(CO)_{11}]$

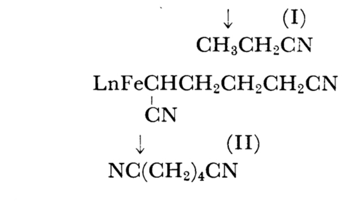
$[NEt_3H][HFe_3(CO)_{11}]$ mmol	CH_3OH m*l*	$ClCH_2CH_2CN$ mmol	AN	Product, mmol PN	ADN
2.5	5	27	0	9.0*	
2.7	5	27	28	4.8	2.3
2.7	5	0	28	2.1	1.2

* In addition to propionitrile 2.8 mmol of acrylonitrile were found.
Reaction conditions: 50°C; 24 hr

the reaction of an appropriate iron carbonyl with a base were prepared and reacted with acrylonitrile. The results, given in Table 2, show that mononuclear iron carbonyl hydrides give the branched hydrodimer, while polynuclear hydrides have a tendency to form the linear one.

Table 3 shows the results of the reaction of acrylonitrile and/or 3-chloropropionitrile with a trinuclear hydride complex, $[NEt_3H][HFe_3(CO)_{11}]$, prepared by the reaction of $Fe(CO)_5$, NEt_3, and H_2O. Propionitrile and acrylonitrile were formed by the reaction of 3-chloropropionitrile with the hydride. The yield of hydrodimers became much larger when acrylonitrile reacted with the hydride in the presence of 3-chloropropionitrile than when only acrylonitrile reacted with the complex. Moreover, when ethyl acrylate reacted with the hydride in the presence of 3-chloropropionitrile, ethyl 5-cyanovalerate was formed in addition to ethyl adipate.

From a consideration of these facts, the following reaction mechanism may be proposed for the hydrodimerization of acrylonitrile, where Ln represents the ligands other than hydrogen;



$$\begin{array}{l} \mathrm{LnFeH} \xrightarrow{\mathrm{CH_2{=}CHCN}} \mathrm{LnFeCH_2CH_2CN} \xrightarrow{\mathrm{CH_2{=}CHCN}} \\ \qquad\qquad\qquad\qquad \downarrow \ \mathrm{(I)} \\ \qquad\qquad\qquad\quad \mathrm{CH_3CH_2CN} \\ \qquad\qquad \mathrm{LnFe}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2CH_2CH_2CN} \\ \qquad\qquad\qquad \downarrow \qquad \mathrm{(II)} \\ \qquad\qquad \mathrm{NC(CH_2)_4CN} \end{array}$$

In the first step, a cyanoethyl complex, I, is formed by the addition of acrylonitrile to a hydride complex. The complex I is also formed by the reaction of 3-chloropropionitrile with a hydride. In this step, the direction of the addition of acrylonitrile to a hydride may determine whether the structure of the hydrodimers is branched or linear. This direction of addition is supposed to depend upon the electronic nature of the hydrogen attached to the transition metal atom and the steric hindrance of the other ligands to the approach of acrylonitrile to the metal-hydrogen bond. In the second step, by the further addition of acrylonitrile to the cyanoethyl complex, I, a dicyanobutyl complex, II, is formed; the hydrodimers are produced from this complex.

Experimental

Treatment of Acrylonitrile with the System Composed of Iron Carbonyl, Alkali, and Water. In a typical experiment, 20 m*l* of benzene, 11 mmol of iron pentacarbonyl, 32 mmol of sodium hydroxide, 140 mmol of water, 300 mmol of acrylonitrile, and 0.3 g of hydroquinone were charged into a 100-m*l* stainless-steel autoclave. After replacing the atmosphere with nitrogen, the mixture was kept at 110°C for 4 hr under 80 atm of nitrogen. The reaction products were then analyzed by gas chromatography. There were found to be 12 mmol of propionitrile, 4.4 mmol of ethylene cyanohydrin, 2.5 mmol of 2-methylglutaronitrile, 7.3 mmol of adiponitrile, and 13 mmol of 2, 2'-dicyanoethyl ether. The conversion of acrylonitrile was 46%. The individual fractions were identified by a comparison of their retention times with those of authentic samples and by collecting vapor-phase-chromatography fractions and a comparison of their infrared and nuclear magnetic resonance spectra with those of authentic samples.

Gas chromatographic analysis was carried out as follows: for the analysis of acrylonitrile and propionitrile, a 3-m dioctyl sebacate solumn was used. The conditions were: column temperature, 70°C; flash evaporator temperature, 150°C; and helium gas speed, 30 m*l*/min. For the analysis of the other products, a 2-m polyoxyethylene sorbitan monooleate column was used, and the conditions were: column temperature, 200°C; inlet temperature, 250°C; and helium gas speed, 80 m*l*/min.

Treatment of Acrylonitrile with the Iron or Cobalt Carbonyl- Sodium Borohydride or -Lithium Aluminum Hydride System or the Cobalt Carbonyl-H_2 System. The treatment of acrylonitrile was carried out as above, and the reaction products were analyzed by gas chromatography.

The Reaction of Acrylonitrile with Salts of Iron Carbonyl Hydrides. The following salts of iron carbonyl hydrides were prepared according to the literature and subjected to reaction with acrylonitrile.

$[\mathrm{Ni}(o\text{-phen})_3][\mathrm{HFe(CO)_4}]_2$[8)]

$[\mathrm{Fe}(o\text{-phen})_3][\mathrm{HFe(CO)_4}]_2$[9)]

$[\mathrm{Ni}(o\text{-phen})_3][\mathrm{HFe_2(CO)_8}]_2$[10)]

$[\mathrm{NEt_3H}][\mathrm{HFe_3(CO)_{11}}]$[11)]

In a typical experiment, 2.1 mmol of the salt $[\mathrm{NEt_3H}]$-$[\mathrm{HFe_3(CO)_{11}}]$ and 45 mg of the polymerization-inhibitor hydroquinone were charged into a Schlenk-type tube under nitrogen, and then 6 m*l* of methanol and 3 m*l* of acrylonitrile were distilled into the reactor under a vacuum. After the reactor had been closed by fusing, the mixture was kept reacting at 50°C for 24 hr. By gas chromatographic analysis, the components were found to be 1.4 mmol of propionitrile and 1.3 mmol of adiponitrile. The conversion of acrylonitrile was 25%.

The Reaction of 3-Chloropropionitrile and Ethyl Acrylate with the Complex $[\mathrm{NEt_3H}][\mathrm{HFe_3(CO)_{11}}]$. The methanol solution of 3-chloropropionitrile and ethyl acrylate was treated with the complex by the procedures described above. Ethyl 5-cyanovalerate and diethyl adipate were found by gas chromatography. The authentic samples were prepared according to the method of Baizer.[12)]

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8) W. Hieber and E. Fach, *Z. Anorg. Allgem. Chem.*, **236**, 83 (1938).

9) W. Hieber and H. Frankel, *Chem. Ber.*, **86**, 710 (1953).

10) W. Hieber and G. Brendel, *Z. Anorg. Allgem. Chem.*, **289**, 324 (1957).

11) J. B. Case and M. C. Whiting, *J. Chem. Soc.*, **1960**, 4632.

12) M. M. Baizer, *J. Org. Chem.*, **29**, 1670 (1964).