

로듐(I)-퍼클로라토 착물을 촉매로 하는 불포화 니트릴의 중합반응

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Polymerization of Unsaturated Nitriles with a Rhodium(I)- Perchlorato Complex

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요 약 : 수소(H_2) 분위기에서, $Rh(ClO_4)(CO)(PPh_3)_2$ (1)가 존재할 때 얻어지는 아크릴로니트릴 (AN)의 소중합체는 올레핀기의 수소를 갖고 있지 않으며, AN 소중합체의 평균소중합도는 약 6이다. 즉 $H(CH_2-CH(CN))_nH$ 이 된다. AN의 소중합은 아래와 같이 추측된다. 즉 $[Rh(CH_2=CHCN)(CO)(PPh_3)_2]^+$ 이 먼저 생성되고, 이것이 H_2 와 반응하여, 디히드ريد로로듐(III)착물, $[Rh(H)_2(CH_2=CHCN)(CO)(PPh_3)_2]^+$ 가 생성된 다음 $[Rh(H)(CH_2CH_2CN)(CO)(PPh_3)_2]^+$ 로 전환된다. 이어서 여러 분자의 AN이 Rh-C 결합에 차례로 삽입되어 $[Rh(H)(CH_2-CH(CN))_nCH_2CH_2CN)(CO)(PPh_3)_2]^+$ 이 생성된 다음 최종적으로 환원성 제거 반응에 의하여 소중합체들이 생성되는 것으로 생각된다. AN 소중합반응의 속도는 AN의 농도를 증가시키면 크게 증가하고, 수소(H_2)의 압력을 증가시키면 약간 증가한다. 따라서, 수소화반응 생성물, CH_3CH_2CN 의 양을 줄이려면 AN의 농도를 높게 하고 수소의 압력을 낮게 해야한다. 수소(H_2) 분위기에서, 착물 1이 존재할 때 일어나는 크로토노니트릴(CRN, $CH_3-CH=CHCN$)소중합반응 속도는 AN의 소중합반응 속도보다 훨씬 느리다. 그러나 한편 CRN의 수소화반응은 AN의 수소화반응보다 빠르다. 이러한 결과는 CRN의 메틸기에 의한 입체적인 효과로 설명할 수 있다.

Abstract: Oligomers of acrylonitrile (AN) obtained in the presence of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) under hydrogen (H_2) do not contain olefinic hydrogen, and the average degree of oligomerization of AN was found to be *ca.* 6 (i.e., $H(CH_2-CH(CN))_nH$). Oligomerization of AN seems to occur via the formation of $[Rh(CH_2=CHCN)(CO)(PPh_3)_2]^+$ which consequently reacts with H_2 to give dihydridorhodium(III) complex, $[Rh(H)_2(CH_2=CHCN)(CO)(PPh_3)_2]^+$ and then $[Rh(H)(CH_2CH_2CN)(CO)(PPh_3)_2]^+$ which undergoes the insertion of a number of $CH_2=CHCN$ molecules into Rh-C bond to produce $[Rh(H)(CH_2-CH(CN))_nCH_2CH_2CN)(CO)(PPh_3)_2]^+$ which finally yields oligomers by reductive elimination. It has been found that an increase in AN concentration drastically increases the rate of oligomerization which is moderately increased by increasing H_2 pressure, and the oligomerization of AN

with 1 should be carried out in higher concentration of AN and lower H_2 pressure to avoid a significant amount of the hydrogenation product, CH_3CH_2CN . Oligomerization of crotonitrile (CRN, $CH_3CH=CHCN$) with 1 under H_2 is significantly slower than that of AN whereas the hydrogenation of CRN is faster than that of AN, which seems to be the results of the steric effect of the methyl group of CRN.

INTRODUCTION

Oligomerization of an olefin is likely to occur in the presence of the metal complex which catalyzes the hydrogenation of the olefin especially when the final step of the hydrogenation, reductive elimination of hydridoalkylmetal group, is comparable in rate with the insertion of another olefin molecule into the metal-alkyl bond (see Scheme I).

It was briefly reported that a significant amount of oligomers is formed during the hydrogenation of unsaturated nitriles and aldehydes (L) to the corresponding saturated nitriles and aldehydes in the presence of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) whose ClO_4 group is so labile that it is readily replaced by L to give $[RhL(CO)(PPh_3)_2]ClO_4$.^{1,2} Oligomerization of unsaturated nitriles and aldehydes with 1 under hydrogen (H_2) is currently under investigation in detail.

In this paper, the oligomerization of acrylonitrile (AN, $CH_2=CHCN$) with 1 under hydrogen is described in detail along with the pertinent data for the oligomerization of crotonitrile (CRN, $CH_3CH=CHCN$).

RESULTS AND DISCUSSION

Oligomers of $CH_2=CHCN$ (AN)

Stirring AN in the absence of 1 under N_2 or H_2 produces practically no oligomers of AN whereas a small amount of oligomers of AN is produced in the presence of 1 under N_2 . 1H NMR spectrum of the oligomers obtained with 1 under N_2 shows olefinic protons at δ 5-6 ppm (relative to TMS). Accordingly, the oligomerization of AN with 1 under N_2 may be explained by the same mechanism suggested in the polymerization of AN with the iridium analogue, $Ir(ClO_4)(CO)(PPh_3)_2$ under

nitrogen.^{3,4} On the other hand, the oligomers of AN obtained under H_2 in the presence of 1 do not contain olefinic protons (see Figure 1), and the hydrogenation of AN to propionitrile also occurs simultaneously in the presence of 1 under H_2 (see below). Therefore, the oligomerization of AN under H_2 with 1 unambiguously occurs through the formation of β -cyanoethylhydridorhodium species, $H-Rh-CH_2CH_2CN$ which undergoes the insertion reaction of $CH_2=CHCN$ molecules to give $H-Rh\{CH-CH(CN)\}_nCH_2CH_2CN$ and then the reductive elimination to produce oligomers, $H\{CH-CH(CN)\}_nCH_2CH_2CN$ (see Scheme I).

Fig. 1 provides valuable information on the nature of the oligomers. The ratio of the signals at δ 0.45 ppm (due to CH_3) and at δ 0.3-3.1 (due to $CHCN$, CH_2 and CH_2CN) is *ca.* 5.6 which indicates the average degree of oligomerization being *ca.* 6 (i.e., $H\{CH_2-CH(CN)\}_6H$). Infrared spectrum (KBr pellet) of the oligomers of AN shows a strong and sharp absorption band at 2220 cm^{-1} due to $C\equiv N$ stretching mode.

Oligomerization of Acrylonitrile (AN) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1) under Hydrogen

Oligomerization and hydrogenation of AN with 1 do not show a change in their rates at least for 24 hours at $30^\circ C$ under hydrogen. The rates of both reactions, thereafter, gradually decrease until they reach about one-hundredth of their initial rates within a week. The isolated rhodium complex from the AN solution of 1 which had been stirred under hydrogen at $30^\circ C$ for 24 hours was identified as $[Rh(CH_2=CHCN)(CO)(PPh_3)_2]ClO_4$ (2) which previously was reported to be formed in the reaction of 1 with AN.¹ The metal complex(es) isolated after *ca.* 40 hours under the catalytic conditions was found to contain a significant amount of unknown rhodium complex

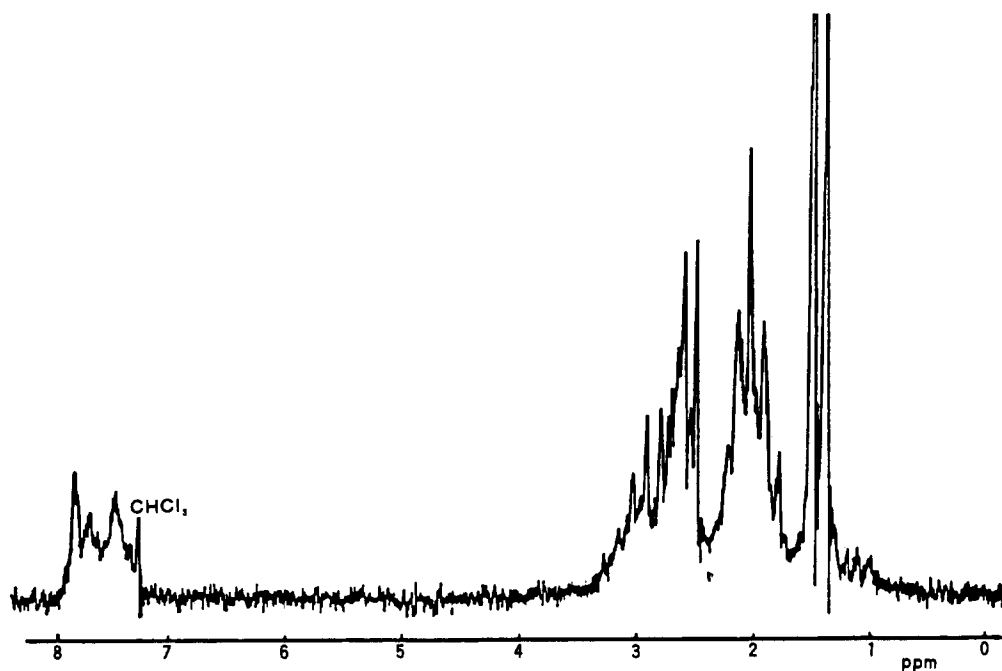


Fig. 1. ^1H NMR spectrum of the non-volatile materials separated from the reaction mixture of $\text{CH}_2=\text{CHCN}$ (10 ml) and $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (0.3 mmole) stirred under hydrogen ($P_{\text{H}_2}=500$ mmHg) at 30°C for 72 hours. Spectrum was obtained using CDCl_3 at 60 MHz. Signals at 7.3-8.0 ppm are due to phenyl protons of PPh_3 coordinated to rhodium.

Table.1 Oligomerization and Hydrogenation of $\text{CH}_2=\text{CHCN}$ with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (1) (0.3 mmole, $[\text{Rh}]=0.03$ M) at 30°C under Hydrogen for the First 24 Hours

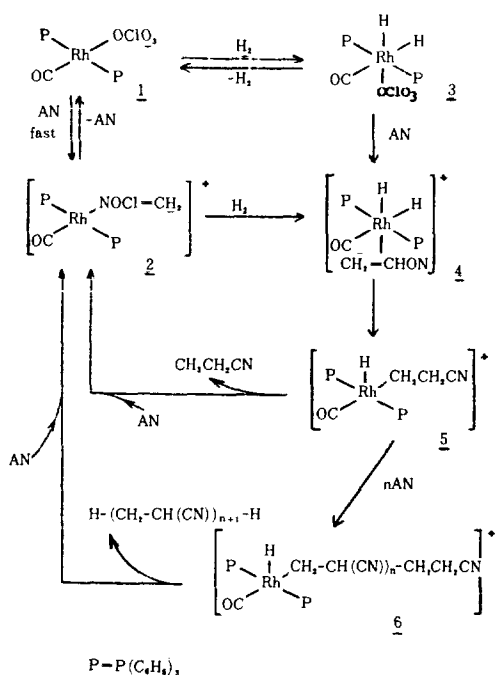
$\text{CH}_2=\text{CHCN}$, M	H_2 (mmHg)	Oligomerization (10^{-5} mole / sec)	Hydrogenation (10^{-5} mole / sec)	Oligomerization Hydrogenation
15.08 ^a	500	16.21	2.55	6.36
7.54 ^b	500	1.39	1.45	0.96
3.77 ^c	500	0.32	1.10	0.29
15.08 ^a	250	6.02	0.95	6.34

^a In neat $\text{CH}_2=\text{CHCN}$ (10 ml). ^b Mixture of $\text{CH}_2=\text{CHCN}$ (5.0 ml) and CDCl_3 (5.0 ml).

^c Mixture of $\text{CH}_2=\text{CHCN}$ (2.5 ml) and CDCl_3 (7.5 ml).

(es). Therefore, it may be said that only the data obtained at the early stage of the catalytic reactions can be discussed quantitatively with respect to the relevant mechanisms involving 1 and 2. Table 1 summarizes the data for the first 24 hours while the deterioration of 1 (or 2) to the unknown compounds is not significant. The

dependence of AN and H_2 on the rates of oligomerization and hydrogenation, respectively does not seem to fit any simple rate equations (see Table 1), which is somewhat expected since both of oligomerization and hydrogenation involve various steps as shown in Scheme 1. Scheme 1 is suggested for the following reasons. (1) Equilibrium between



Scheme 1. Suggested mechanism for the oligomerization and hydrogenation of $\text{CH}_2=\text{CHCN}$ with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (1) under hydrogen.

1 and 2 was already established in our study.¹ (2) Equilibrium between 1 and 3 was also previously reported.⁵ (3) Coordination of AN to rhodium should occur through the olefinic group in order to undergo the hydrogenation to give propionitrile and the oligomerization to give oligomers containing no olefinic groups but nitrile groups. Accordingly, complex 4 is an inevitable intermediate. (4) Complex 5 and 6 are consequent species which finally eliminate the products of hydrogenation and oligomerization, respectively.

Reaction of 1 with AN to give 2 is very fast (too fast to measure the rate), and the equilibrium constant for the reaction, $1 + \text{AN} \rightleftharpoons 2$ is very large ($5.61 \times 10^4 \text{ M}^{-1}$ at 30°C).¹ It has been found in our experiments that the reaction of 1 with 2 to give 3 is negligible, i.e., the electronic absorption of 1 under N_2 (prominent absorption band at 350 nm) is practically same with that under H_2 . It

is, therefore, reasonable to assume that the catalytic reactions proceed mainly through $1 \rightarrow 2 \rightarrow 4 \rightarrow 5 (\rightarrow 6)$. It should be mentioned that complex 1 also react with the hydrogenation product, propionitrile to give $[\text{Rh}(\text{CH}_3\text{CH}_2\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ where $\text{CH}_3\text{CH}_2\text{CN}$ is coordinated to rhodium through the nitrogen atom but not through the π -system of the nitrile group,⁶ and that the dissociation of ClO_4^- group from 1 to give three coordinated $\text{Rh}(\text{CO})(\text{PPh}_3)_2^+$ is negligible at 25°C .¹ Although the data for the reaction rates in Table 1 may not be quantitatively explained with respect to the suggested mechanism in Scheme I, the followings are the results obtained in this study. (1) Increasing AN concentration drastically increases the rate of oligomerization but only moderately increases the rate of hydrogenation. (2) Increase in H_2 concentration significantly increases the rates of both reactions. (3) The ratio of the rate of oligomerization to that of hydrogenation greatly increases as AN concentration increases while it does not seem to depend on H_2 concentration. Accordingly, it may be safely said that oligomerization should be carried out in highly AN concentration and lower H_2 concentration to avoid a significant amount of the hydrogenation product, $\text{CH}_3\text{CH}_2\text{CN}$.

Oligomerization of Crotonitrile (CRN) with $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (1) under Hydrogen

Complex 1 also catalyzes the hydrogenation (to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$) and oligomerization of $\text{CH}_3\text{CH}=\text{CHCN}$ (CRN, mixture of *cis* and *trans* isomer, *cis/trans* = 1.0) under hydrogen at 30°C . ^1H NMR spectrum of the oligomers obtained does not show signals due to olefinic protons. Unlike for the oligomers of AN, the degree of oligomerization of CRN can not be simply determined by ^1H NMR spectrum of CRN oligomers since all the signals of the oligomers spread in the region of 1-2 ppm. Infrared spectrum (KBr pellet) of CRN oligomers shows a medium-intensity absorption band at 2220 cm^{-1} due to $\text{C}\equiv\text{N}$ stretching vibration. Under N_2 in the presence of 1, no oligomers of CRN were obtained at 30°C for several days.

It was already known that complex 1 reacts with CRN to give $[\text{Rh}(\text{CH}_3\text{CH}=\text{CHCN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (7) and the equilibrium constant for the reaction, $1+\text{CRN} \rightleftharpoons 7$ is also very large ($2.93 \times 10^5 \text{ M}$).¹ It is, therefore, assumed that the hydrogenation and oligomerization of CRN with 1 follow the same reaction pathways suggested in Scheme I. The hydrogenation and oligomerization of CRN with 1 also do not show a change in rates at 30°C under hydrogen for 36 hours after which the rates of both reactions gradually decrease but continue for several days.

Table 2 summarizes the data obtained for the first 24 hours of the catalytic reactions of CRN with 1. These data again do not seem to fit any simple rate equations. It is noticed in Table 2 that the hydrogenation is much faster than the oligomerization for CRN while both of the reactions occurs in comparable rates for AN under the conditions employed in this study (see Table 1). This observation is readily understood by the relative easeness of the insertion of CRN and AN molecules into Rh-C bond of Rh-CH-(CN)CH₂CH₃ (or Rh-CH(CH₃)CH₂CN) and Rh-CH₂CH₂CN, respectively in a standpoint of steric effect. While the insertion of CRN into Rh-C bond may not be so facile because of the methyl group, the reductive elimination of CH₃CH₂CH₂CN (hydrogenation product) may be facilitated by the methyl group. The insertion of AN into Rh-C bond may not be so difficult as that of CRN while the reductive elimination of Rh(H)(CH₂CH₂-

CN) to yield CH₃CH₂CH₂CN (hydrogenation product) may not be so fast due to the lack of the methyl group as that of Rh(H)(CH(CN)-CH₂CH₃) to CH₃CH₂CH₂CN.

EXPERIMENTAL

¹H NMR and infrared spectra were measured on Varian 60 MHz (Model EM-360A) and Shimadzu IR-440 instruments. CH₂=CHCN (Aldrich) and CH₃CH=CHCN (mixture of *cis* and *trans* isomers, *cis/trans*=1.0) (Aldrich) were distilled in vacuum before use. H₂ (high purity) was purchased from Dong Yang Argon Co. and used without further purification. Rh(ClO₄)(CO)(PPh₃)₂ was prepared by the literature method.⁷

Oligomerization and Hydrogenation of Acrylonitrile (AN) and Crotononitrile (CRN)

Since the practically same procedure was followed in all experiments, experimental details for the reactions of 1 in neat AN (15.08 M) are described below for an example. A 50 ml round-bottom flask with one side arm (stopped with a rubber cap) containing Rh(ClO₄)(CO)(PPh₃)₂ (0.22 g, 0.3 mmole) was connected to the vacuum system whose total volume was *ca.* 3.0 liter, and evacuated. Then H₂ was introduced into the system until the pressure reached 500 mmHg. A 10 ml of CH₂=CHCN saturated with H₂ at 30°C was added into the flask by a syringe through the rubber cap. The pressure of the system reached *ca.* 640 mmHg (vapor pressure of CH₂=CHCN at 30°C

Table 2. Hydrogenation and Oligomerization of CH₃CH=CHCN (mixture of *cis* and *trans* isomers, *cis/trans*=1.0) with Rh(ClO₄)(CO)(PPh₃)₂ (1) (0.3 mmole, [Rh]=0.03 M) at 30°C under Hydrogen for the First 24 Hours

CH ₃ CH=CHCN, M	H ₂ (mmHg)	Oligomerization (10 ⁻⁵ mole / sec)	Hydrogenation (10 ⁻⁵ mole / sec)	Oligomerization Hydrogenation
12.30 ^a	500	0.33	11.80	0.028
6.15 ^b	500	0.24	6.75	0.036
3.08 ^c	500	0.19	2.70	0.063
12.30 ^a	250	0.30	8.12	0.037

^a In neat CH₃CH=CHCN (10 ml). ^b Mixture of CH₃CH=CHCN (5.0 ml) and CDCl₃ (5.0 ml).

^c Mixture of CH₃CH=CHCN (2.5 ml) and CDCl₃ (7.5 ml).

is 133 mmHg^o) within 10 minutes, which was maintained throughout the measurements while the reaction mixture was stirred at 30°C on a thermostat. A part (0.5 ml) of the reaction mixture was taken out of the reaction flask at intervals of 5-6 hours and analyzed by ¹H NMR measurements. The ratio of total moles of AN and PPh₃ (coordinated to rhodium) to total moles of CH₃CH₂CN and AN oligomers was determined by the signals at 5-7 ppm (due to AN and PPh₃) and 1-3 ppm (due to CH₃CH₂CN and AN oligomers). The volatile materials were separated from the reaction mixture (after ¹H NMR measurement) by using a dry-ice/acetone trap. The mole ratio of AN to CH₃CH₂CN was determined by the signals at 5-7 ppm (due to AN) and 1-3 ppm (due to CH₃CH₂CN) of the spectrum of the volatile materials, and that of PPh₃ to AN oligomers was determined by the signals at 6-7 ppm (due to PPh₃) and 1-3 ppm (due to AN oligomers) of the spectrum of the non-volatile materials. The ratio of AN : CH₃CH₂CN : AN oligomers in mixture was determined in the way described above.

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