

균일 촉매반응 (제 2 보). 트란스-클로로카르보닐비스(트리페닐포스핀)이리듐 (I)에 의한 아크릴로니트릴의 수소화반응

文致章 · 陳宗權†

서강대학교 이공대학 화학과  
(1982. 4. 30 접수)

Homogeneous Catalysis (II). Hydrogenation of Acrylonitrile with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium (I)

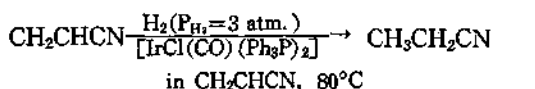
Chi Jang Moon and Chong Shik Chin†

Department of Chemistry, Sogang University Seoul 121, Korea

(Received April 30, 1982)

A four coordinated iridium complex known as Vaska's compound, *trans* [IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>] (Ph<sub>3</sub>P=triphenylphosphine) (I), reacts reversibly with molecular hydrogen and acrylonitrile, respectively, at room temperature in most organic solvents.<sup>1</sup> Accordingly, the iridium complex I is expected to show catalytic activities for the reactions such as hydrogenation, polymerization and hydroformylation of acrylonitrile. To our knowledge, there has never been a report on the hydrogenation of acrylonitrile by an iridium complex.

In this note we wish to report a catalytic hydrogenation of acrylonitrile to propionitrile<sup>2</sup> with the iridium complex I in solution (equation 1). At room temperature, no evidence was obtained for the hydrogenation. At above 80°C, however, the hydrogenation (equation 1) proceeds fairly rapidly (see below for the rate of the hydrogenation).



(1)

In a typical experiment, the compound 1 (0.10 g, 0.13 mmole) was dissolved at room temperature in 5.0 ml (76 mmole) of acrylonitrile in a 400 ml stainless steel reactor designed for the reactions under high pressure. Then the reaction mixture was flushed with hydrogen several times to remove oxygen from the reactor and reaction mixture, and kept under hydrogen ( $P_{\text{H}_2}=3 \text{ atm.}$ ) at room temperature for few minutes. The reactor was finally put in a oven thermostated at 80°C. A portion of the solution was taken at intervals for <sup>1</sup>H-NMR measurements from the reactor after cooling the reactor to room temperature and lowering the hydrogen pressure to one atmosphere by means of a needle valve attached to the reactor.

Fig. 1 shows that propionitrile (CH<sub>3</sub> at 1.1 ppm (relative to TMS) as a triplet, CH<sub>2</sub> at 2.2 ppm as a quartet) is produced from the hydrogenation of acrylonitrile in the presence of the iridium complex I. The ABC pattern of acrylonitrile (unreacted) is seen at ~6 ppm. The signals around 7.6 ppm are due to the phenyl

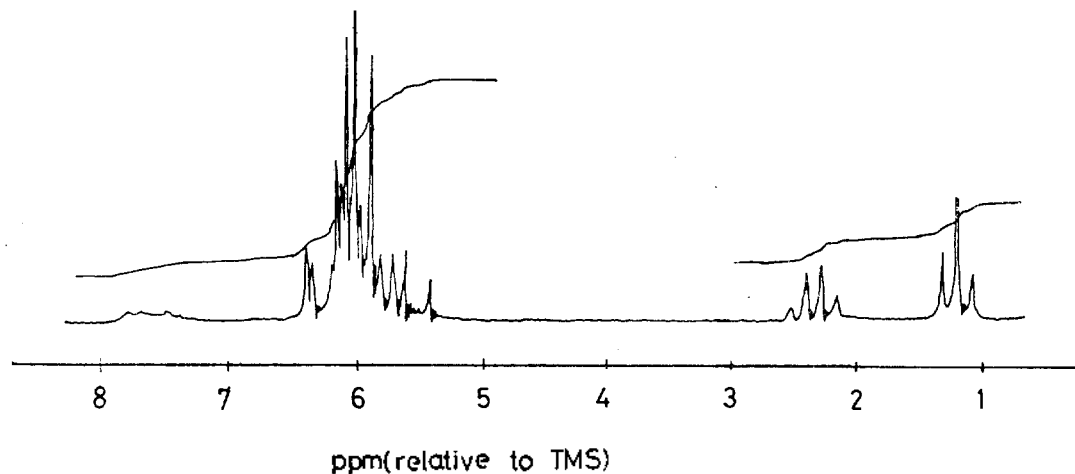


Fig. 1.  $^1\text{H-NMR}$  spectrum of the reaction mixture of acrylonitrile and  $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  (1) after heating at  $80^\circ\text{C}$  for 28 hours under hydrogen ( $P_{\text{H}_2}=3 \text{ atm.}$ ) (see text for experimental detail).

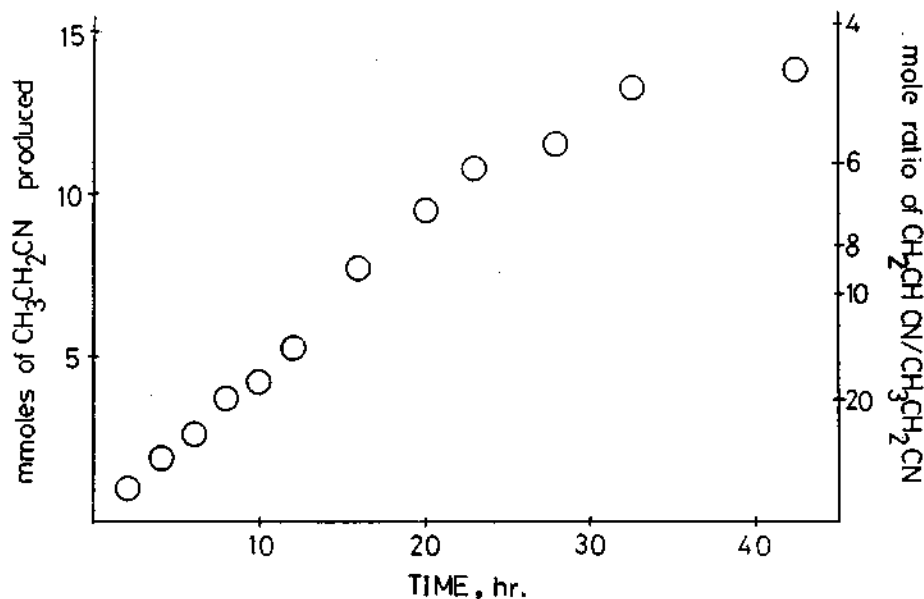


Fig. 2. The rate of the hydrogenation versus reaction time at  $80^\circ\text{C}$  under  $P_{\text{H}_2}=3 \text{ atm.}$  0.1 g of  $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$  (1) (0.13 mmole) and 5.0 ml of acrylonitrile (76 mmole) were initially used (see text for experimental detail).

hydrogens of triphenylphosphine ligands coordinated to iridium. The blank tests confirmed that propionitrile is not produced without the iridium complex 1, and no solid material was

observed during the reaction<sup>3</sup> (the reaction mixture was a clearly pale yellow solution), which indicate that the hydrogenation is a homogeneous catalysis by the iridium complex 1.

Fig. 2 shows the extent of the hydrogenation with the reaction time, where a significant induction period is not seen. It is noticed that the rate of the hydrogenation is nearly constant for the first 30 hours until the mole ratio of  $\text{CH}_2\text{CHCN}:\text{CH}_3\text{CH}_2\text{CN}$  reaches to approximately 6:1, and then decreases gradually. Since the hydrogenation was carried out in neat acrylonitrile solution at first and propionitrile produced was not separated at all from the reaction mixture during the hydrogenation to obtain the data given in Fig. 2, the concentration of acrylonitrile would decrease gradually as the hydrogenation proceeds. Therefore, the decrease in the rate of the hydrogenation may be due to the decrease in concentration of acrylonitrile.

In order to obtain information on the mechanism of the catalysis, the reaction mixture obtained (after heating for four hours under the catalytic conditions and cooling down to room temperature) was dried in an open flask with bubbling hydrogen into the solution to yield light yellow solid (2), which was washed with hexane. The light yellow solid 2 is very soluble in acrylonitrile and chloroform and very slightly soluble in benzene and carbon tetrachloride. The solid 2 does not seem to be a single compound (see reference 4 for the spectral data of 2). Attempts to purify the solid 2 have been thus far unsuccessful. Although the infrared and  $^1\text{H-NMR}$  spectra do not lend a simple formulation for the light yellow solid 2,<sup>4</sup> those may suggest that the solid 2 is a mixture of  $[\text{Ir}(-\text{CH}_2\text{CH}_2\text{CN})(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]$  (3),<sup>4,5</sup> other hydridocarbonyliridium

complex(es)<sup>4a</sup> and probably small amount of acrylonitrile oligomers.<sup>4</sup>

It is interesting to notice that the compound 3 has been expected to be an intermediate in the homogeneous catalyses such as hydrogenation and polymerization.<sup>6</sup>

#### ACKNOWLEDGEMENTS

This study is a part of the "Selective Reduction" supported by the Korean Ministry of Education.

#### REFERENCES

1. L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968) and the references therein.
2.  $^1\text{H-NMR}$  measurements clearly show that  $\text{CH}_2\text{CH}_2\text{CN}$  is the only product of the hydrogenation of  $\text{CH}_2\text{CHCN}$ , *i.e.*,  $\text{CH}_2\text{CHCH}_2\text{NH}_2$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  was not observed (see Fig. 1).
3. A small amount of oily acrylonitrile oligomers was observed after longer reaction time. Detailed experimental results will be published elsewhere.
4. (a) Infrared spectrum of the solid 2 in KBr disc shows two  $\nu_{\text{CO}}$  at  $1965\text{ cm}^{-1}$  (very strong) and  $2040\text{ cm}^{-1}$  (medium), one  $\nu_{\text{C-H}}$  at  $2170\text{ cm}^{-1}$  (strong), one  $\nu_{\text{CN}}$  at  $2205\text{ cm}^{-1}$  (medium), one  $\delta_{\text{H-H}}$  at  $830\text{ cm}^{-1}$  (weak), several  $\nu_{\text{C-H}}$  at  $2880\text{ cm}^{-1}$  (weak), and most  $\text{Ph}_3\text{P}$  bands; (b)  $^1\text{H-NMR}$  spectrum of the solid 2 in  $\text{CDCl}_3$  shows the phenyl hydrogens in  $\text{Ph}_3\text{P}$  coordinated to iridium at  $\sim 7.6$  ppm (relative to TMS), and three sets of multiplets at  $\sim 4.1$ ,  $\sim 2.3$  and  $\sim 1.3$  ppm. The ratio of the peaks is approximately 30 ( $\sim 7.5$  ppm): 0.6 ( $\sim 4.1$  ppm): 3 ( $\sim 2.3$  ppm): 6 ( $\sim 1.3$  ppm).
5. The infrared spectrum of  $[\text{Ir}(-\text{CH}_2\text{CH}_2\text{CN})(\text{CH}_2\text{CHCN})(\text{CO})(\text{Ph}_3\text{P})_2]$  (3) showed  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  at 1965 and  $2205\text{ cm}^{-1}$ , respectively.<sup>6</sup>
6. W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969).