NOTES

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Further Study on the Course of Olefin Dimerization Catalyzed by σ-Aryl Nickel(II) Compound-Boron Trifluoride Etherate

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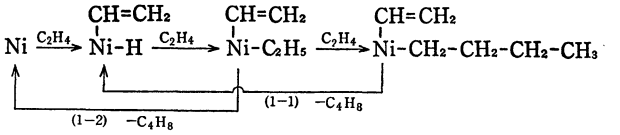
The codimerization of ethylene with propylene catalyzed by the catalyst systems composed of bis(triphenylphosphine)bromo(σ-aryl)nickel(II) and boron trifluoride etherate was investigated to know the course of the reaction from the product distribution. 2-Pentene and 2-methyl-1-butene are mainly formed in the first stage of the codimerization. Their formations are in consistent with the process of the insertion of propylene into ethyl-nickel bond to form 1-methylbutyl- and 2-methylbutyl-nickel complexes followed by elimination of β-hydrogen to give 2-pentene and 2-methyl-1-butene respectively.

It was reported that a new catalyst system composed of a σ-aryl nickel(II) compound and boron trifluoride etherate is highly active and selective for ethylene dimerization1) and the codimerization of ethylene with styrene2) to give butene and 3-phenyl-1-butene respectively. From the study on the isotopic exchange between C_2H_4 and C_2D_4 and the dimerization of C_2D_4 using this catalyst system, it has been concluded that a nickel hydride is responsible for dimerization of ethylene and that the hydrogen is supplied by dissociative addition of ethylene.3) In the previous paper,4) two possible processes(1–1 and 1–2) were left undiscriminated on the course of dimerization of ethylene with the same catalyst.



$$Ni \xrightarrow{C_2H_4} \overset{CH=CH_2}{\overset{|}{Ni}}\text{-}H \xrightarrow{C_2H_4} \overset{CH=CH_2}{\overset{|}{Ni}}\text{-}C_2H_5 \xrightarrow{C_2H_4} \overset{CH=CH_2}{\overset{|}{Ni}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

The isomer distribution of pentene obtained from the codimerization of ethylene with propylene, however, is helpful to discriminate them, because the isomer distribution of pentene formed depends on the processes expected for 1–1 and 1–2.

The present work was undertaken to clarify the course of olefin dimerization catalyzed by bis(triphenylphosphine) bromo(1-naphthyl)nickel(II) in the presence of boron trifluoride etherate by investigating the product distribution of the codimerization of ethylene with propylene.

Experimental

Dried bis(triphenylphosphine)bromo(1-naphthyl)nickel (II) (1 mmol) prepared according to the method described in the literature5) was dissolved in a dried methylene dichloride (30 ml) at 0°C under nitrogen atmosphere, using a two necked flask (50 ml), followed by adding a given amount of benzene solution of purified boron trifluoride etherate (10% in volume) with vigorous stirring. The nitrogen in the flask was, then, evacuated before propylene (300 ml at S. T. P.) was introduced into the flask at 0°C and the pressure was kept constant at 40 cmHg for a given period of time by supplying ethylene during the run. The codimerization was terminated by cooling the flask with liquid nitrogen. All volatile materials such as ethylene, propylene, butenes, pentenes, solvent *etc.* in the flask were transferred into another flask cooled with liquid nitrogen and their amounts were determined by a gas chromatograph equipped with VZ-7 columun (8 m).

Results and Discussion

The mole ratio of propylene to ethylene in the solution was separately estimated from their solubilities in methylene dichloride under the same condition. On addition of propylene (300 ml S. T. P.) to the methylene dichloride solution(30 ml) of $1\text{-}C_{10}H_7Ni(P\phi_3)_2Br$ in the absence of boron trifluoride etherate, 249 ml of propylene was dissolved leaving a 20 cmHg of propylene in the gas phase. On a further addition of ethylene to this solution up to a total pressure of 40 cmHg including 20 cmHg of propylene and 15 cmHg of the solvent vaper, 13 ml (S. T. P.) of ethylene was dissolved. Thus the mole ratio, C_3H_6/C_2H_4, in the solution is calculated to be about 23, a fairly large excess of propylene. This ratio could be assumed to be unchanged during the early period of the reaction time. Since ethylene was absorbed almost linearly with respect to the reaction time, the rate of ethylene absorption was obtained from its amount consumed within a given reaction time. This rate can be regarded as the rate of reaction of ethylene under large excess of propylene dissolved. The rate increases linearly with increasing the mole ratio as was observed in the dimerization of ethylene.4) In Fig. 1, the product distribution at the same temperature and concentrations of ethylene and propylene are plotted against the amount of ethylene consumed, which depends on the reaction time and the mole ratio of $BF_3 \cdot OEt_2$ to $1\text{-}C_{10}H_7Ni(P\phi_3)_2Br$. This indicates that the product distribution neither depends on the amount of ethylene consumed, nor on the mole ratio of the catalyst. Accordingly, both butene and pentene are catalytically formed by the same active species and its amount increases almost

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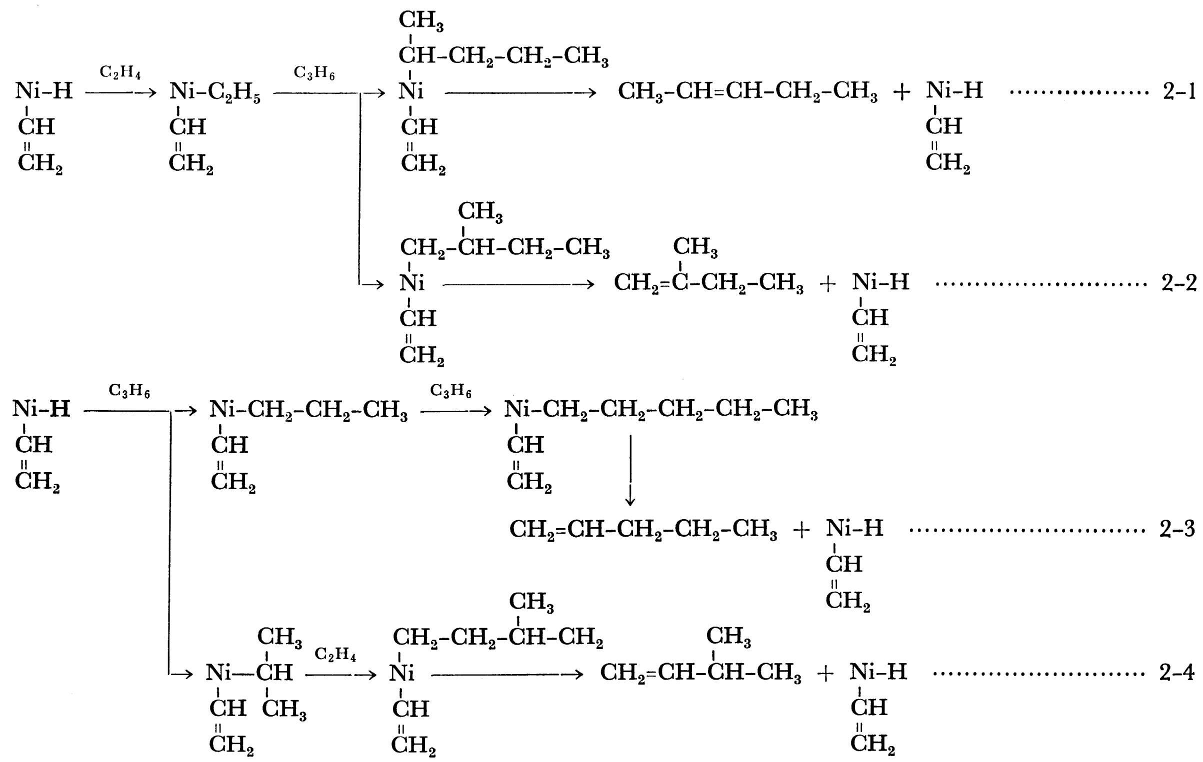
1) K. Maruya, T. Mizoroki, and A. Ozaki, This Bulletin, **43**, 3630 (1970).

2) N. Kawata, K. Maruya, T. Mizoroki, and A. Ozaki, *ibid.*, **44**, 3217 (1971).

3) K. Maruya, T. Kuroki, T. Mizoroki, and A. Ozaki, *ibid.*, **44**, 2002 (1971).

4) K. Maruya, T. Mizoroki, and A. Ozaki, *ibid.*, **45**, 2255 (1972).

5) J. Chatt, and B. L. Show, *J. Chem. Soc.*, **1960**, 1718.



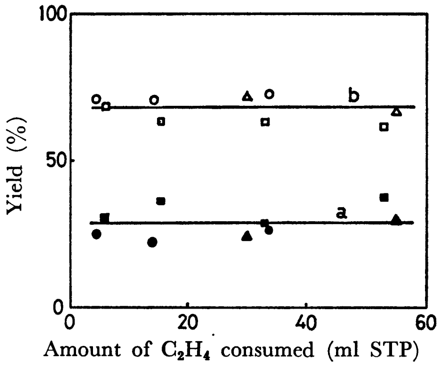


Fig. 1. Yields of butene and pentene based on the amount of ethylene consumed.
a: pentene, b: butene, ●,○: $BF_3 \cdot OEt_2$ 0.8 mmol, ■,□: $BF_3 \cdot OEt_2$ 1.6 mmol, △,▲: $BF_3 \cdot OEt_2$ 2.4 mmol

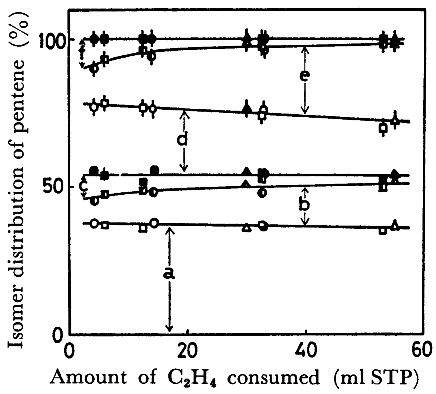


Fig. 2. Product distribution of the codimerization of ethylene with propylene.
a: 2-methyl-1-butene, b: 2-methyl-2-butene, c: 3-methyl-1-butene, d: *cis*-2-pentene, e: *trans*-2-pentene, f: 1-pentene. ○,◐,●,ϕ,ϕ,ϕ: $BF_3 \cdot OEt_2$ 0.8 mmol, □,◧,■,ф,ф,ф: $BF_3 \cdot OEt_2$ 1.6 mmol, △,◭,▲,△,◭,▲: $BF_3 \cdot OEt_2$ 2.4 mmol

linearly with increasing the amount of boron trifluoride etherate as was discussed in the previous paper.[4] The isomer distribution of pentene is shown in Fig. 2 as a function of the amount of ethylene consumed. The initial products of the codimerization are mainly 2-pentene and 2-methyl-1-butene. The fraction of isopentene in total pentene is nearly 54±1%, independent of the amount of ethylene consumed and the mole fraction of the catalyst. Since the sum of the selectivities to butene and pentene reaches near 100%, a secondary reaction of butene and pentene with ethylene is negligible. The coordination equilibrium between olefin and the active species is evidently more favorable for ethylene than for propylene, because butene is preferably formed even in the presence of a large excess of propylene. This is also supported by the strong inhibition of the dimerization of propylene caused by ethylene.

If pentene is formed through the following processes (2-1∼4) expected for 1-1, four isomers of pentene, 2-methyl-1-butene, 1-pentene and 3-methyl-1-butene, will be initially formed. If it does through the other processes expected for 1-2, neither 2-pentene, nor 2-methyl-1-butene will be initially formed. Figure 2 indicates that pentene should be formed predominantly through the processes of 2-1∼4, since 2-pentene (d and e) and 2-methyl-1-butene(a) are main products, where the formation of small amounts of 1-pentene and 3-methyl-1-butene can be attributed to the disadvantage of propylene for its coordination to the active species of the catalyst. Thus this results supports that butene is formed through the process of 1-1. At present, there is no evidence to support the existence of vinyl ligand on nickel atom during the reaction. All attempts to detect the vinyl and its coupling compounds were unsuccessful.