Dimerization of C_2D_4 Catalyzed by Bis(triphenylphosphine)-σ-1-naphthyl Nickel (II) Bromide

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(Received April 3, 1971)

It has been reported that bis(triphenylphosphine)σ-arylnickel (II) bromide catalyzes the selective dimerization of ethylene in the presence of boron trifluoride etherate in dry methylene chloride or benzene solution.[1] This catalyst system contains no substance such as alkylaluminum[2] or alkyllithium which is likely to provide a nickel hydride. We must clarify whether ethylene dimerization is catalyzed by a nickel hydride formed during the reaction and what substance supplies the hydrogen to the nickel complex if the nickel hydride is formed. For this purpose we studied the isotopic exchange between C_2H_4 and C_2D_4 and between C_2D_4 and other chemical species involved in the reaction system of the dimerization.

The isotopic exchange of C_2H_4–C_2D_4 (1:1) was carried out at 0°C for 5 or 10 min, using bis(triphenylphosphine)σ-1-naphthyl nickel (II) bromide (0.20 mmol) in the presence of boron trifluoride etherate (0.29 or 0.72 mmol) in dry methylene chloride (10 m*l*). Concurrent dimerization of ethylene was observed as follows.

$BF_3(Et_2O)$	Reaction time	Conversion	$1\text{-}C_4'$	*trans*-$2\text{-}C_4'$	*cis*-$2\text{-}C_4'$
0.29 mmol	10 min	46.5%	56	30	14
0.72 mmol	5 min	55.8%	29	50	21

In either case the isotopic distribution in the residual ethylene was C_2H_4 7%, C_2H_3D 26%, $C_2H_2D_2$ 37%, C_2HD_3 24% C_2D_4 6%, which was in good agreement with equilibrium distribution. This result shows that the rate of isotopic exchange is strikingly faster than the ethylene dimerization, and that one hydrogen atom is exchanged in one act of the exchange. Thus it is concluded that there must be an active hydrogen atom which catalyzes the exchange reaction. In this case, the active hydrogen atom is very likely provided as a nickel hydride.

The source of the active hydrogen was examined by the reaction of C_2D_4 (atomic fraction of hydrogen f_H=0.020). The reaction condition was the same as in the above reaction. The results are shown in Table 1.

Table 1. Atomic fraction of hydrogen (f_H) in ethylene or butene after the reaction of C_2D_4

No.	Ni complex (mmol)	BF_3OEt_2 (mmol)	CH_2Cl_2 (m*l*)	C_2D_4 introduced	React. time	f_H
1	0.20	0.79	10	1.16	3 hr	0.022[a)]
2	0.20	0.72	10	1.00	10 hr	0.024[a)]
3	0.20	0.72	10	1.13	150 hr	0.023[a)]
4	0.20	0.72	30	1.10	5 min	0.020[b)]
5	1.0	0.72	30	1.09	5 min	0.020[b)]
6	2.0	0.72	30	1.07	5 min	0.021[b)]
7	1.0	3.6	30	1.06	5 min	0.020[a)] 0.020[b)]
8	2.0	7.2	30	1.11	5 min	0.022[b)]

a) Calculated from the butene formed.
b) Calculated from the residual ethylene.

If the active hydrogen comes from the solvent or the ligand, the atomic fraction of hydrogen in ethylene or butene formed should be higher than that in the starting material (f_H=0.020). However, no appreciable increase in f_H is observed as shown in Table 1, independent of the reaction time, the amount of catalyst, and the amount of solvent, while the amount of C_2D_4 is approximately fixed. This means that no hydrogen is supplied to the nickel complex from the solvent, triphenylphosphine, 1-naphthyl ligand or diethyl ether

It is concluded that the isotopic exchange and the dimerization of ethylene is catalyzed by a nickel hydride complex which is formed by the reaction of ethylene with the nickel complex.

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

[2] M. Uchino, Y. Chauvin, and G. Lefebvre, *C. R. Acad. Sci., Paris, Ser.* **265**, 103 (1967).