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Isotopic Exchange in C_2D_4–C_2H_4 and in D_2–H_2 Catalyzed by Bis(triphenylphosphine)-Nickel(II) Halide

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Bis(triphenylphosphine)-nickel(II) halide has been found to catalyze the H–D exchange reaction of C_2D_4 and C_2H_4 in the presence of molecular hydrogen at room temperature in spite of the fact that the rate of the exchange between H_2 and D_2 is very slow. From the kinetics of this reaction and the solvent effect, it has been postulated that bis(triphenylphosphine)-nickel(II) halide forms a nickel–hydride complex by the heterolytic splitting of hydrogen molecule in the course of the reaction as follows:

$$NiX_2(P\phi_3)_2 + H_2 \rightarrow NiHX(P\phi_3)_2 + HX$$

where X and ϕ are halogen and C_6H_5, respectively. The nickel hydride complex thus formed is concluded to be the real catalyst for the H–D exchange in ethylene by the scheme.

$$C_2D_4 + NiH \rightarrow NiC_2D_4H \rightarrow C_2D_3H + NiD$$

It has been reported that square planar complexes of d^8 transition metals such as $IrX(CO)(P\phi_3)_2$ (X = halogen; $\phi = C_6H_5$) (*1*) and $RhX(P\phi_3)_3$ (*2*) are transformed to hydride complexes by the reaction with molecular hydrogen and thus may be used as a catalyst for the hydrogenation of olefin. The platinum complex, $PtCl_2(P\phi_3)_2$, which has the same electronic configuration as the above, is converted to $PtHCl(P\phi_3)_2$ by the reaction with molecular hydrogen (*3*). The former hydride complexes are admittedly formed by dissociative addition or homolytic splitting of hydrogen, whereas the latter is formed by a heterolytic splitting of hydrogen.

Regardless of their ways of formation, all of these hydrides are stable and isolatable, while the formation of nickel hydride complex by the treatment of a nickel(II) compound with hydrogen has not yet been reported. Recently, Itatani and Bailer have shown that bis(triphenylphosphine)-nickel(II) halides promote the isomerization and hydrogenation of methyl linolate in benzene or tetrahydrofuran at 90°C under 30 atm of hydrogen pressure (*4*). Many σ-organo-nickel(II) complexes of the types, $NiRX(PR'_3)_2$ and $NiR_2(PR'_3)_2$ (R and R′ = alkyl or aryl), were obtained by treating $NiX_2(PR'_3)_2$ with Grignard reagents or organo-lithium compounds at low temperature, although they were unstable and could not be isolated when R is alkyl (*5*). Furthermore, it was reported that the treatment of $NiX_2(PR_3)_2$ with some suitable reducing agents results in the formation of a complex whose infrared (*6*) and nmr spectra (*7*) may be assigned to nickel hydride, $NiHX(PR_3)_2$. Recently it was reported that a stable yellow brown crystal of $NiHCl[P(C_6H_{11})_3]_2$ is obtained from the reaction of $NiCl_2[P(C_6H_{11})_3]_2$ with $NaBH_4$ at room temperature (*8*).

These facts suggest that $NiX_2(PR_3)_2$ can also activate molecular hydrogen forming a hydride complex, which can be converted into a σ-alkyl complex in the presence of an olefin. In agreement with this prediction, it has been found that the H–D exchange reaction between C_2D_4 and C_2H_4 really takes place in the presence of molecular hydrogen and $NiX_2(PR_3)_2$ as the catalyst at room temperature.

The present work deals with C_2D_4–C_2H_4 and H_2–D_2 exchange reactions catalyzed by $NiX_2(PR_3)_2$.

Experimental

(1-1) *Preparations of Ni(II) and Co(II) Complexes*

Nine complexes of the type of MX_2L_2 ($M = Ni$, Co; $X = Cl$, Br, I, SCN; $L = P\phi_3$, $P(C_2H_5)_3$) were prepared by the methods described in literatures (*4, 9–11*). Di-iodo-bis(triphenylphosphite)-nickel(II), $NiI_2[P(O\phi)_3]_2$, was prepared by the reaction of an equimolar mixture of bis(triphenylphosphite)-nickel dicarbonyl, $Ni(CO)_2[P(O\phi)_3]_2$ and iodine in an anhydrous diethyl ether under nitrogen atmosphere. The product was obtained as a brown crystal by washing well with anhydrous diethyl ether (Analysis: C, 45.77; H, 3.22; I, 28.1; Ni, 6.4%. Calculated for $C_{36}H_{30}O_6I_2NiP_2$: C, 46.3; H, 3.24; I, 27.2; Ni, 6.30%).

(1-2) *Reactants*

Deuteroethylene was prepared by deuteration of C_2D_2 at room temperature over a Girdler (58A) Pd catalyst. C_2D_2 was obtained by reaction of D_2O with CaC_2 which had been preevacuated at 400°C for 150 hr. The D concentration in the deuteroethylene was 93–97%. Deuterium gas was obtained by the electrolysis of D_2O and dried by liquid nitrogen trap. The D concentration in the gas was 96.5%. Organic solvents were freed from water mostly by reaction with metallic sodium followed by distillation.

(1-3) *Procedure; C_2D_4–C_2H_4 and H_2–D_2 Exchange Reactions*

The reaction vessel was a simple flask of 68 ml which was connected to a vacuum line and to a nitrogen line. The catalyst complex and solvent were admitted into the flask under the atmosphere of O_2-free dry nitrogen. The nitrogen in the flask had been evacuated to 10^{-2} mm before the reactant gases were introduced into it. The temperature of the catalyst solution was maintained at 35 ± 0.2°C with magnetic stirring. Analyses of the reaction products were made by mass spectrometry with an ionization voltage of 10 V.

Results

(2-1) *C_2D_4–C_2H_4 Exchange Reaction by $MX_2(PR_3)_2$*

A number of runs of the exchange reaction between C_2D_4 and C_2H_4 were carried out by nickel(II) or cobalt(II) complexes as the catalyst using a 1:1 mixture of C_2H_4 and C_2D_4 in the presence of hydrogen. The amounts of ethylene (0.7 mmol), hydrogen (0.4 mmol) and the catalyst (0.15 mmol) placed in the reaction vessel (68 ml) were kept constant. The reaction time was ranged from 80 min to 48 hr, depending on the magnitude of the reaction rate.

Results are shown in Table 1. It can be seen that the isotopic mixing in ethylene does not take place in the absence of hydrogen, although a small amount of deuterium was lost in 48 hr, probably into solvent or phosphine. The extent of isotopic mixing in ethylene, x, is defined as

$$x = \frac{M_{00} - M_{0t}}{M_{00} - M_{0e}} \qquad (1)$$

where M_{00}, M_{0t} and M_{0e} denote the mole fractions of d_0 species, C_2H_4, at time 0, t and equilibrium respectively. M_{0e} is calculated by $(1 - f_D)^4$, where f_D is the atomic fraction of deuterium in the total ethylene, M_{0e} being 0.070 for (*A*), 0.078 for (*B*), 0.066 for (*C*) and 0.072 for (*D*). The values of x are shown in Table 1. The atomic D fractions of the ethylene produced are nearly equal to those of starting materials. In agreement with this observation, only trace amount of HD was detected in hydrogen. It can be accordingly concluded

TABLE 1

C_2D_4–C_2H_4 EXCHANGE REACTION BY MX_2L_2 IN THE PRESENCE OF HYDROGEN

Run	Catalyst	Solv	Time (hr)	H_2 (mmol)	[a]	Ethylene produced (%) d_4	d_3	d_2	d_1	d_0	f_D	x
1	$NiBr_2(P\phi_3)_2$	C_6H_6	48	—	A	41.3	5.1	2.2	1.0	50.4	46.4	—
2	$NiBr_2(P\phi_3)_2$	THF	48	—	A	41.5	5.2	2.1	0.8	50.4	46.7	—
3	$NiCl_2(P\phi_3)_2$	C_6H_6	1.33	0.54	A	44.0	5.9	0.2	0.1	49.8	48.5	—
4	$NiBr_2(P\phi_3)_2$	C_6H_6	1.33	0.33	A	35.0	13.1	2.9	8.8	40.2	49.5	22.8
5	$NiBr_2(P\phi_3)_2$	C_6H_6	3	0.33	A	17.4	23.4	16.6	18.7	23.9	47.9	60.7
6	$NiI_2(P\phi_3)_2$	C_6H_6	1.33	0.38	A	34.0	14.6	2.7	8.0	40.7	48.3	21.6
7	$NiI_2(P\phi_3)_2$	C_6H_6	3	0.38	B	13.0	21.9	19.9	19.6	25.6	44.3	57.4
8	$NiI_2\{P(O\phi)_3\}_2$	C_6H_6	1.5	0.33	C	27.9	18.7	8.6	15.4	29.4	50.0	42.5
9	$NiBr_2(P\phi_3)_2$	THF	1.33	0.43	A	32.6	16.1	3.6	9.9	37.8	49.0	28.4
10	$NiBr_2(P\phi_3)_2$	THF	3	0.43	C	10.8	23.6	30.3	22.3	13.0	49.2	85.2
11	$NiI_2(P\phi_3)_2$	THF	1.33	0.42	A	7.4	24.0	31.9	25.3	11.4	47.6	89.8
12	$Ni(SCN)_2(P\phi_3)_2$	THF	48	0.48	B	37.7	10.8	2.0	0.8	49.3	47.0	—
13	$NiBr_2(PEt_3)_2$	THF	48	0.42	B	23.1	19.0	7.2	12.4	30.3	44.1	46.4
14	$NiI_2(PEt_3)_2$	THF	48	0.33	B	5.3	19.9	35.0	29.9	10.5	45.2	93.0
15	$NiI_2\{P(O\phi)_3\}_2$	THF	1.33	0.35	C	48.1	2.4	0.7	0.4	48.4	50.3	—
16	$CoCl_2(P\phi_3)_2$	THF	1.33	0.43	D	41.7	7.5	0.7	0.4	49.7	47.8	—
17	$CoBr_2(P\phi_3)_2$	THF	1.33	0.37	D	43.1	7.7	0.3	0.2	48.8	49.1	—
18	$CoI_2(P\phi_3)_2$	THF	1.33	0.43	D	42.8	7.2	0.5	0.4	49.1	48.5	—

Catalyst, 0.15 mmol; Solvent, 25 ml; Total ethylene, 0.70 mmol; Reaction temp., 35°C.

[a] The deuterium distribution (%) of starting ethylene:

	d_4	d_3	d_2	d_1	d_0	f_D		d_4	d_3	d_2	d_1	d_0	f_D
A	44.0	6.0	—	—	50.0	48.5	C	47.5	2.5	—	—	50.0	49.4
B	38.0	10.2	1.1	—	50.7	46.2	D	43.0	7.2	—	—	50.0	48.2

that the added hydrogen plays a role as a cocatalyst rather than a reactant.

As indicated by the value of x, the catalytic effectiveness of the nickel(II) complexes increases in the order Cl $\ll$ Br $\leqq$ I in both benzene and THF, while no exchange was observed with any cobalt(II) complex.

$NiI_2[P(O\phi)_3]_2$ gave the highest effectiveness in benzene solvent as shown in Table 1. This complex decomposed slightly in benzene and some black precipitate was observed inside the reaction vessel, whereas the removal of the precipitate had no effect on the exchange reaction rate. On the other hand, $NiI_2[P(O\phi)_3]_2$ showed no catalytic effectiveness in THF solvent, where no precipitate was formed.

(2-2) *Rate Analysis for the C_2D_4–C_2H_4 Exchange Reaction*

The result shown in Table 1 indicates that one hydrogen atom is exchanged in one act of the exchange. In such a case, the probability of exchange with deuterium is given by the atomic deuterium fraction in total ethylene, f_D, and that with protium by $(1 - f_D)$. Since little change in f_D was observed in the runs shown in Table 1, it may be assumed that f_D is constant at the initial value through the run. Now, let us define R, the rate of isotopic mixing in ethylene, which may be a function of C_E (conc. of total ethylene), C_{H_2} (conc. of hydrogen) and temperature. When M_0, M_1, M_2, M_3, and M_4 are the mole fractions of d_0, d_1, d_2, d_3, and d_4 ethylenes, respectively, the rates of formation of each deutero species are given by Eq. (2).

$$dM_4/dt = \frac{R}{C_E}\left\{-(1 - f_D)M_4 + \frac{1}{4}f_D M_3\right\},$$

$$dM_3/dt = \frac{R}{C_E}\left\{(1 - f_D)M_4 - \frac{1}{4}(3 - 2f_D)M_3 + \frac{1}{2}f_D M_2\right\},$$

$$dM_2/dt = \frac{R}{C_E}\left\{\frac{3}{4}(1-f_D)M_3 - \frac{1}{2}M_2 + \frac{3}{4}f_D M_1\right\},$$

$$dM_1/dt = \frac{R}{C_E}\left\{\frac{1}{2}(1-f_D)M_2 - \frac{1}{4}(1+2f_D)M_1 + f_D M_0\right\},$$

$$dM_0/dt = \frac{R}{C_E}\left\{\frac{1}{4}(1-f_D)M_1 - f_D M_0\right\} \quad (2)$$

Since R and C_E are constant in each run,

$$\frac{R}{C_E}\,dt = d\left(\frac{Rt}{C_E}\right)$$

and thus Rt/C_E can be denoted by A for simplification:

$$\mathrm{A} = Rt/C_E$$

The Mi-A relations were obtained by solving those equations numerically by means of an electronic computer. One of the results is shown in Fig. 1, where the initial values of Mi are $M_0 = 0.5$, $M_1 = M_2 = 0$, $M_3 = 0.06$ and $M_4 = 0.44$ corresponding to an f_D value of 0.485. If the assumptions made for Eq. (2) are appropriate, the observed value of Mi at a definite reaction time of a run should be given on the curves of Fig. 1 at a definite value of A. In this way Eq. (2) may be examined for its validity. Plots are exemplified on the curves. A little better agreement is obtained by adopting $f_D = 0.475$ instead of 0.485. This means that a small amount of deuterium is lost into molecular hydrogen or solvent. Anyway, the value of A for a run can be estimated as a mean value of A's obtained from Mi utilizing those curves.

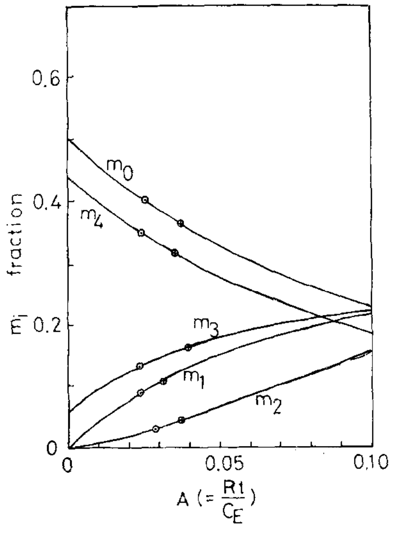

FIG. 1. Mi calculated from Eq. (2).

(2-3) *The Rate Expression for Isotopic Mixing in Ethylene Promoted by $NiBr_2(P\phi_3)_2$*

The exchange runs were carried out at 35°C varying reaction time in the presence of different amount of hydrogen using $NiBr_2(P\phi_3)_2$ in benzene (30 ml) and a fixed amount of ethylene (0.8 mmol). The extent of reaction, A, in these runs can be estimated from the observed value of Mi at time t, utilizing the curve shown in Fig. 1. The values of A thus obtained are plotted against time in Fig. 2, where it is shown that the exchange reaction has an induction period which is shortened with increase in hydrogen pressure. Figure 3 is the log-log plot of A/t ($=R/C_E$) against the amount of hydrogen, where the values of A/t were obtained from the slopes of linear part of lines in Fig. 2. The result of Fig. 3 may be expressed by the relation:

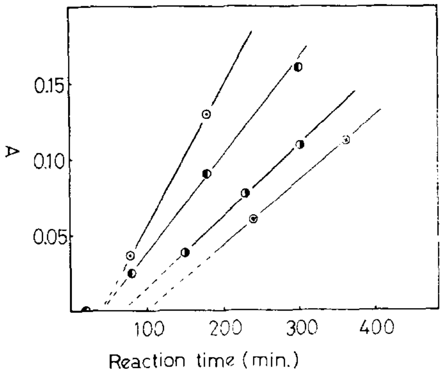

FIG. 2. Effect of hydrogen pressure on the reaction rate $NiBr_2(P\phi_3)_2$, 0.15 mmol; total ethylene, 0.70 mmol; benzene, 30 ml; ⊙, H_2 = 0.61 mmol; ◐, H_2 = 3.3 mmol; ◑, H_2 = 0.24 mmol; ◉, H_2 = 0.20 mmol.

$$R/C_E \propto [C_{H_2}]^{0.65} \qquad (3)$$

Another series of runs of the exchange reaction were carried out with various amounts of ethylene (0.40 ~ 0.85 mmol) at 35°C for 80 min in the presence of a fixed amount of H_2 (0.33 mmol). The result is shown in Fig. 4, which indicates that A ($=Rt/C_E$) is nearly independent of the amount of ethylene.

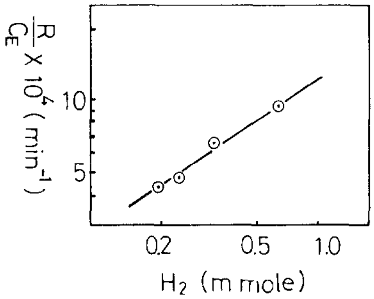

FIG. 3. Plots of A/t against the amount of hydrogen (log-log scale).

In summary the rate expression for the isotopic mixing of ethylene in the presence of hydrogen catalyzed by $NiBr_2(P\phi_3)_2$ in benzene is given by Eq. (4).

$$R = kC_EC_{H_2}^{0.65} \qquad (4)$$

(2-4) Solvent Effect on the C_2D_4-C_2H_4 Exchange Reaction

The effect of solvent was tested by adding the second solvent to benzene, the amount of which was one-half of benzene by volume. The catalyst was $NiX_2(P\phi_3)_2$ (X = Br,I). Other experimental conditions were the same as those described in the section (2-1). The results are shown in Table 2. The rate of exchange reaction by $NiI_2(P\phi_3)_2$ is remarkably increased by adding polar and basic solvents such as anisole and THF. Ethanol, a more polar solvent, however, decreased the rate, perhaps because of the decomposition of the nickel(II) complex (9). The solvent effect was less significant for $NiBr_2(P\phi_3)_2$.

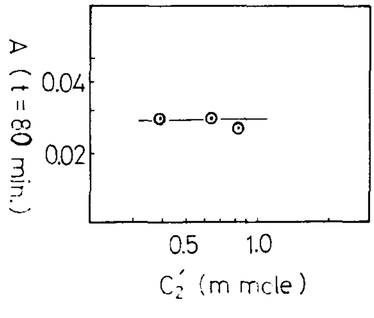

FIG. 4. Independence of A of the amount of ethylene (log-log scale).

(2-5) D_2-Olefin Exchange Reaction

As described in the section (2-1), it has been found that hydrogen acts as a cocatalyst of $NiX_2(P\phi_3)_2$ in the C_2D_4-C_2H_4 exchange reaction and that the exchange between hydrogen and ethylene is much slower than the isotopic mixing between ethylene molecules. Further runs of D_2-olefin exchange were made with propylene, 1-butene and butadiene at 35°C for 48 hr using $NiBr_2(P\phi_3)_2$ in benzene. The results are shown in Table 3, where no significant difference is observed among the extents of exchange of monoolefins, suggesting that the rate of exchange between hydrogen and olefin is determined by the step of hydrogen activation.

TABLE 2
EFFECT OF SOLVENT

Run	Catalyst	Solvent	x
1	$NiI_2(P\phi_3)_2$	C_6H_6[a]	21.6
2	$NiI_2(P\phi_3)_2$	C_6H_6-xylene[b]	14.7
3	$NiI_2(P\phi_3)_2$	C_6H_6-naphthalene[c]	20.1
4	$NiI_2(P\phi_3)_2$	C_6H_6-diethyl ether[b]	18.4
5	$NiI_2(P\phi_3)_2$	C_6H_6-anisole[b]	43.7
6	$NiI_2(P\phi_3)_2$	C_6H_6-THF[b]	88.6
7	$NiI_2(P\phi_3)_2$	THF[a]	89.8
8	$NiBr_2(P\phi_3)_2$	C_6H_6[a]	22.8
9	$NiBr_2(P\phi_3)_2$	C_6H_6-diethyl ether[b]	23.5
10	$NiBr_2(P\phi_3)_2$	C_6H_6-THF[b]	46.5
11	$NiBr_2(P\phi_3)_2$	C_6H_6-ethanol[b]	~0

Catalyst, 0.15 mmol; Total ethylene, 0.70 mmol; H_2, 0.40 mmol; Temp., 35°C; Time, 80 min.

[a] Benzene or THF, 30 ml.

[b] A mixture of C_6H_6 (20 ml) and the other solvent (10 ml).

[c] $C_{10}H_8$ (5 g) was dissolved in C_6H_6 (30 ml).

(2-6) D_2-H_2 Exchange Reaction

The exchange reaction between H_2 and D_2 (total amount, ~1 mmol) were carried

TABLE 3
D_2-OLEFIN EXCHANGE REACTION

Reaction	Hydrogen mmol	Olefin mmol	Hydrogen (%)			Olefin (%)		
			d_2	d_1	d_0	$d_{2\sim\infty}$	d_1	d_0
Starting material			93.5	6.1	0.4	—	—	100
D_2-C_2H_4	0.33	0.86	81.7	11.1	7.2	—	5.0	95.0
D_2-C_3H_6	0.39	0.86	86.7	8.4	4.9	—	3.0	97.0
D_2-1-C_4H_8	0.45	0.87	86.8	7.3	5.9	—	4.2	95.8
D_2-C_4H_6	0.41	0.82	89.7	9.8	0.5	—	~1	~99

Catalyst, $NiBr_2(P\phi_3)_2$, 0.15 mmol; Benzene, 30 ml; Temp., 35°C; Time, 48 hr.

TABLE 4
H_2–D_2 EXCHANGE REACTION

Run	Catalyst NiX_2L_2	Solvent	Hydrogen mmol		Mol. fraction (%)			f_D %	x'
					D_2	HD	H_2		
1	X = Br, L = $P\phi_3$	THF	0.59	[a]	57.8	3.7	38.5	59.7	~0
				[b]	57.7	4.0	38.3	59.7	
2	Br, $P\phi_3$	C_6H_6	0.77	[a]	53.0	3.4	43.6	54.7	10.2
				[b]	49.0	8.1	42.9	53.1	
3	I, $P\phi_3$	THF	0.91	[a]	37.9	2.4	59.7	39.1	15.2
				[b]	32.7	9.4	57.9	37.4	
4	I, $P\phi_3$	THF + C_2H_4[c]	1.00	[a]	46.9	3.0	50.1	48.4	2.6
				[b]	40.9	4.2	54.9	43.0	
5	I, $P\phi_3$	C_6H_6	1.06	[a]	46.8	2.9	50.4	48.3	56.1
				[b]	28.1	29.3	42.6	42.8	
6	I, $P\phi_3$	C_6H_6 + $C_{10}H_8$[d]	1.03	[a]	45.8	2.9	51.3	47.3	46.6
				[b]	20.0	24.8	55.2	32.4	
7	I, $P\phi_3$	C_6H_6 + $C_{14}H_{10}$[e]	1.00	[a]	46.8	3.0	50.2	48.3	52.2
				[b]	22.9	27.5	49.6	36.7	
8	I, $P\phi_3$	C_6H_6 + C_2H_4[c]	0.99	[a]	49.6	3.2	47.2	51.2	58.2
				[b]	15.7	30.4	53.9	30.9	
9	I, $P\phi_3$	C_6H_6 + C_2H_4[c]	1.09	[a]	45.1	2.9	52.0	46.5	21.6
		+$C_{10}H_8$		[b]	24.6	13.0	62.4	31.1	
10	I, $P\phi_3$	C_6H_6 + $C_{10}H_{18}$[f]	1.05	[a]	45.6	2.9	51.5	47.1	58.4
				[b]	28.0	30.3	41.7	43.2	
11	I, PEt_3	THF	1.02	[a]	47.3	3.0	49.7	48.8	~0
				[b]	47.4	3.1	49.5	48.9	
12	I, PEt_3	C_6H_6	1.09	[a]	49.6	3.1	47.3	51.2	7.9
				[b]	46.1	6.8	47.1	49.5	
13	I, $P(O\phi)_3$	C_6H_6	0.98	[a]	46.9	3.0	50.1	48.4	3.8
				[b]	44.8	4.8	50.4	47.2	

[a] Starting composition.
[b] Product.
[c] C_2H_4, 0.2 mmol.
[d] $C_{10}H_8$, 5 g.
[e] $C_{14}H_{10}$ 1 g.
[f] $C_{10}H_{18}$, 6 ml.
NiX_2L_2, 0.15 mmol: Benzene or THF, 30 ml: Temp., 35°C: Time, 48 hr.

out at 35°C for 48 hr using $NiX_2(P\phi_3)_2$ in benzene or THF. The results are shown in Table 4, where x' denotes the extent of isotopic mixing in hydrogen, i.e.,

$$x' = \frac{M'_0 - M'_t}{M'_0 - M'_e} \qquad (5)$$

where M'_0, M'_t and M'_e denote the mole fractions of HD at time 0, t and equilibrium, respectively. As indicated by the value of x', the isotopic mixing in hydrogen is faster in benzene than in THF and the iodo compound is more effective than bromo-one. It should be noted, however, that as shown by the decrease in the atomic deuterium fraction in molecular hydrogen, a certain part of deuterium was lost from molecular hydrogen increasing with the extent of x'. The loss of deuterium was particularly remarkable when naphthalene or anthracene was added to benzene. But the addition of decahydronaphthalene did not give any appreciable effect.

DISCUSSION

(3-1) The Role of Hydrogen in C_2D_4–C_2H_4 Exchange Reaction

It has been found in this study that the exchange reaction between C_2H_4 and C_2D_4 is promoted by $NiX_2(PR_3)_2$ only in the presence of molecular hydrogen. This result suggests that the hydrogen molecule plays an important role in this catalysis. On the other hand, as shown by the predominant formation of d_1 or d_3 species of ethylene, one hydrogen atom is exchanged in one act of the exchange. Accordingly the hydrogen molecule seems to react with $NiX_2(PR_3)_2$ to form a metal hydride as previously suggested for isomerization or hydrogenation of olefin promoted by metal complex in homogeneous system.

There are two possible ways of metal hydride formation from molecular hydrogen, (*12*) i.e., (1) dissociative addition of hydrogen (2) heterolytic splitting of hydrogen. The former seems to take place favorably with metal complexes of lower oxidation states such as Rh(I) (*13*), Ir(I) (*14*), and Os(O) (*15*), while the latter has been found with metal complexes of higher oxidation states such as Ru(II) (*16*) and Pt(II) (*3*) in polar solvents. In the case of Ni(II) complex, the dihydride complex is not known while the monohydride complex is (*6–8*).

Accordingly the nickel–hydride complex in the present study is most likely formed from the heterolytic splitting of hydrogen molecule as follows:

$$NiX_2(PR_3)_2 + H_2 \rightarrow NiHX(PR_3)_2 + HX \qquad (6)$$

Since this splitting results in the formation of hydrogen halide, the hydride formation would be more favorable in a polar solvent than in nonpolar one (*12*). The solvent effect on the rate of isotopic mixing in ethylene presented in Table 2 is consistent with this prediction. That is, a polar solvent such as THF seems to be effective because it stabilizes the active species $NiHX(PR_3)_2$,* whereas a more polar solvent such as ethanol is ineffective because it decomposes the complex.

The mechanism of the exchange reaction in the presence of metal hydride seems to be indisputable. Ethylene reacts with the hydride forming an ethyl intermediate as follows:

$$C_2H_4 + NiDX(PR_3)_2 \rightarrow NiC_2H_4DX(PR_3)_2 \rightarrow NiHX(PR_3)_2 + C_2H_3D, \qquad (7)$$

thus resulting in the exchange reaction in ethylene.

In summary, the role of hydrogen molecule in this exchange reaction seems to lie in providing the nickel(II) hydride by way of heterolytic splitting. The nickel hydride may also be supplied by the reaction with LiC_2H_5. A preliminary experiment showed that the exchange reaction in ethylene in the presence of LiC_2H_5, instead of hydrogen, took place rapidly with $NiI_2(P\phi_3)_2$ at 35°C, without reduction of the nickel complex.

(3-2) The Rate of Exchange in Ethylene

As mentioned before, little change in f_D of ethylene was observed in the runs shown

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* The solvent effect may also be interpreted in terms of the effect on the transition state of the reaction, but it is hard to discriminate the kinetic effect from the thermodynamic one.

in Table 1. This result demonstrates that only a small amount of deuterium in ethylene was lost into coexistent molecular hydrogen or solvent molecule. Actually HD was hardly detected in those runs as mentioned before, indicating that the exchange reaction in ethylene proceeds much faster than that between ethylene and hydrogen. This was proved in the run shown in Table 3. Only 5% C_2H_3D was formed in 48 hr in the exchange reaction between D_2 and C_2H_4 by $NiBr_2(P\phi_3)_2$, whereas the extent of isotopic mixing in ethylene reached 60% in 3 hr under the same condition.

The exchange reaction between D_2 and C_2H_4 as mentioned above can be effected by reactions (6) and (7), with the former being rate determining in this process. The induction period observed for the exchange in ethylene can be regarded as the time required to form nickel hydride via the slow reaction (6). The observed reduction in the induction period with increase in hydrogen pressure supports this view. It may be accordingly concluded that the reaction (7) is much faster than the reaction (6).

The rate of reaction (7) should be proportional to the concentrations of nickel hydride and ethylene. The steady state value of the former is determined by the equilibrium (6) with the equilibrium constant K,

$$K = \frac{(\mathrm{NiH})(\mathrm{HX})}{(\mathrm{NiX})(\mathrm{H_2})} \qquad (8)$$

where NiH and NiX denote the hydride and the original complexes, respectively. If the concentration of HX is equal to that of NiH as expected from Eq. (6), the concentration (NiH) is given by

$$(\mathrm{NiH}) = \{k(\mathrm{NiX})(\mathrm{H_2})\}^{\frac{1}{2}} \propto (H_2)^{\frac{1}{2}} \qquad (9)$$

where it is assumed that the amount of NiH is much less than that of NiX. The rate of reaction (7), R, is consequently expressed as

$$R \propto (\mathrm{H_2})^{0.5}(\mathrm{C_2H_4})^{1.0} \qquad (10)$$

which is approximately in agreement with the observed kinetics, (4), of the exchange in ethylene.

(3-3) The Isotopic Mixing in Hydrogen and Accompanied Loss of Deuterium

The isotopic mixing in hydrogen was also observed with the same catalyst as shown in Table 4 by the decrease in H_2 fraction, although the rate of mixing was slow. This isotopic mixing in hydrogen may take place by way of the reaction (6), provided that NiH and HX are independent in the solution as assumed in (8). However, the reaction (6) does not explain the loss of deuterium shown in Table 4. There must be another reaction involved in this exchange reaction.

As is pointed out in the results, the loss of deuterium depends on the solvent used and is most pronounced in the solvent containing anthracene or naphthalene, which are known to exchange their hydrogen readily with hydrogen halides (*17*). Accordingly, the deuterium may be transferred to the solvents by way of an exchange reaction (11):*

$$\mathrm{DX} + \mathrm{C}_n\mathrm{H}_m \rightarrow \mathrm{HX} + \mathrm{C\ H}_{m-1}\mathrm{D} \qquad (11)$$

Since the reactivity sequence of aromatic hydrocarbons in the reaction (11) has been assessed as

anthracene $\simeq$ naphthalene $\gg$ benzene,

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* There might be another way of exchange to cause the deuterium loss as follows:

$$\mathrm{NiD} + \mathrm{C}_n\mathrm{H}_m \rightarrow \mathrm{NiH} + \mathrm{C}_n\mathrm{H}_{m-1}\mathrm{D} \qquad (a)$$

This reaction (a). is essentially the same as the reaction (7) which has been discussed to be the main path of the exchange in ethylene. The runs 8 and 9 in Table 4 were made in the presence of ethylene in order to discriminate (a) from (11). The comparison of the runs 6 and 8 with 5 shows that both naphthalene and ethylene increase the loss in f_D. If these two results were caused by a same reaction path, (11) or (a), the isotopic distribution of hydrogen would be unchanged in the presence of both of ethylene and naphthalene. There is, however, a drastic decrease in the amount of HD formation as observed in the run 9. This result may be interpreted as, the deuterium in NiD is lost into ethylene and that in DX into naphthalene, thus reducing HD and increasing H_2. Accordingly the deuterium loss via (a) may be ruled out in the absence of ethylene.

the observed increase in the deuterium loss from benzene to naphthalene or anthracene is reasonably understood from the scheme based on the reaction (11).

In summary, the results obtained in the exchange between H_2 and D_2 can be interpreted in terms of the heterolytic splitting of hydrogen by the nickel complexes, thus supporting the previously described mechanism of ethylene exchange.

(*3-3*) *Ligand Effect*

The ligand effect on the rate of isotopic exchange in ethylene is qualitatively described in (*2-1*). In order to reexamine this effect, the rate constant (k) of Eq. (4) is estimated and shown in Table 5. It is seen that the effect is remarkable in THF, while obscure in benzene, and that the chlorine ligand is ineffective. The relative rates for the different combination of ligands in THF may be summarized as follows:

$$\frac{\mathrm{I}-\phi}{\mathrm{I}-\mathrm{Et}} = \frac{\mathrm{Br}-\phi}{\mathrm{Br}-\mathrm{Et}} \fallingdotseq 20$$

and

$$\frac{\mathrm{I}-\mathrm{Et}}{\mathrm{Br}-\mathrm{Et}} = \frac{\mathrm{I}-\phi}{\mathrm{Br}-\phi} \fallingdotseq 10.$$

It is accordingly concluded that phenyl phosphine is 20 times as effective as that of ethyl phosphine, and that iodine is 10 times as that of bromine. It is also suggested in Table 1 that phosphite is more effective than phosphine. Thus the following sequences of ligand effect may be assessed: For phosphine, $P(O\phi)_3 > P\phi_3 > P(Et)_3$; for halogen, $I > Br > Cl$. These two sequences are opposed in electron-attracting nature of ligand. It is suggested that the role of ligand is different between phosphine and halogen.

The effect of halogen may appear in two ways, namely as a thermodynamic effect in the reaction (6) and as a kinetic effect in the reaction (7). The former effect may be estimated from the relative enthalpy change for the reaction,

$$\mathrm{NiX_2 + H_2 \rightarrow NiHX + HX} \qquad (12)$$

which can be estimated from dissociation energies for the following reactions:

$$\mathrm{NiX_2 \rightarrow NiX + X,} \qquad (13\text{-}1)$$

$$\mathrm{HX \rightarrow H + X,} \qquad (13\text{-}2)$$

$$\mathrm{H_2 \rightarrow 2H,} \qquad (13\text{-}3)$$

$$\mathrm{NiHX \rightarrow NiX + H.} \qquad (13\text{-}4)$$

An available datum (*18*) shows that the reaction (12) is ~7 kcal more favorable with Br than with Cl, assuming an equal value of dissociation energy for (13-4). Corresponding data for iodide is not available, but the data of other metal halides suggests that the reaction (12) is much more favorable with iodide. Thus the ligand effect of halogen seems to be interpretable as a thermodynamic effect in the reaction (6).

The ligand effect by phosphine seems to result from the kinetic effect in the reaction (7). An explanation for the kinetic

TABLE 5

THE RATE CONSTANT (k) OF EQ. (4)

Catalyst	Solv	H_2 (mmol)	React time (hr)	$\frac{R}{C_E \cdot C_{H_2}^{0.65}} \times 10^2$ (hr^{-1})
$NiCl_2(P\phi_3)_2$	C_6H_6	0.54	5	—
$NiBr_2(P\phi_3)_2$	C_6H_6	0.33	3	6.2
$NiI_2(P\phi_3)_2$	C_6H_6	0.38	3	6.9
$NiI_2P(O\phi_3)_2$	C_6H_6	0.33	1.5	8.0
$NiBr_2(PEt_3)_2$	THF	0.42	48	0.18
$NiI_2(PEt_3)_2$	THF	0.33	48	1.9
$NiBr_2(P\phi_3)_2$	THF	0.43	1.33	4.0
$NiI_2(P\phi_3)_2$	THF	0.42	1.33	36

effect may be made on the basis of dπ-electron-accepting nature of the ligand, because the two sequences of the ligand effect both run parallel with this nature of the ligand. Indeed, stabilization of metal–alkyl has been claimed to result from π-coordination of the metal atom (*5*). It seems probable to promote the reaction (7) by stabilization of nickel-ethyl intermediate. Possibly both the thermodynamic and kinetic effects are operative in the overall reaction of the isotopic exchange.

It has been reported by Uchino, Chauvin and Lefebvre (*19*), that the $NiX_2(PR_3)_2$ complex mixed with $Al(C_2H_5)_2Cl$ exhibits a remarkably high activity for the dimerization of propylene at room temperature, giving a dimer distribution controlled by the phosphine ligand but not by the halogen ligand. The selectivity of the propylene dimerization promoted by such nickel complex catalysts has been correlated to the Taft constant σ^* of the substituent group of the phosphine (*19*, *20*). Thus as far as the phosphine ligand is concerned, the controlling factor in the ligand effect observed with the isotopic exchange in ethylene seems to be similar to that of propylene dimerization.

This similarity would be reasonable because both reactions are believed to proceed via the nickel-alkyl intermediate, although the activation of $NiX_2(PR_3)_2$ is made in different ways, one by the reaction with hydrogen and the other with $Al(C_2H_5)_2Cl$. Such a similarity must be originated from the common nature of both reactions that the reactions involve an intermolecular transfer of hydrogen. It seems that the nickel hydride complex which is effective for the isotopic exchange is converted to the dimerization catalyst by cooperation with the acid component such as aluminum halide. This problem will be the subject of the following study.

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