Title	HYDROGEN EXCHANGE BETWEEN HYDROGEN, ETHYLENE OR ETHANE DURING THE PROGRESS OF THE CATALYZED HYDROGENATION OF ETHYLENE IN THE PRESENCE OF NICKEL
Author(s)	MATSUZAKI, Isao; NAKAJIMA, Tsuyoshi
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HYDROGEN EXCHANGE BETWEEN HYDROGEN, ETHYLENE OR ETHANE DURING THE PROGRESS OF THE CATALYZED HYDROGENATION OF ETHYLENE IN THE PRESENCE OF NICKEL

By

Isao MATSUZAKI[*] and Tsuyoshi NAKAJIMA[*]

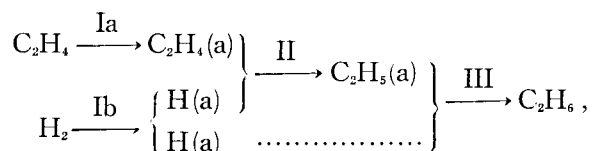(Received March 13, 1965)

Abstract

Hydrogen exchange of the title in the temperature range from 50 to 150°C was theoretically investigated on the basis of the associative mechanism put forward by HORIUTI and POLANYI, concluding that the extent of the exchange was out of the mass spectrometric detection.

The catalyzed interaction between P_2, C_2P_4 and C_2H_6-d (approximately of 30% D content)[**] each of 10 mmHg partial pressure was now observed at 50, 100 and 150°C in the presence of nickel wire in order to check the above conclusion.

No migration of deuterium from ethane to hydrogen or to ethylene was observed, which verified the above theoretical conclusion but the absence of whatever mechanism operative as well, which caused the migration.

Introduction

The experimental findings[1][2], that ethane-deuterium[**] exchange occurs on nickel in the temperature range from 0 to 150°C, have suggested the possibility of the hydrogen atoms in emerging from ethane into hydrogen or ethylene during the progress of the catalyzed hydrogenation of ethylene in the presence of nickel, whereas HORIUTI[3][4] inferred qualitatively that the associative mechanism[5] could hardly give rise to the above exchange; the associative mechanism is represented schematically as

$$C_2H_4 \xrightarrow{\text{Ia}} C_2H_4(a) \left.\begin{array}{c} \\ \end{array}\right\} \xrightarrow{\text{II}} C_2H_5(a) \left.\begin{array}{c} \\ \end{array}\right\} \xrightarrow{\text{III}} C_2H_6 ,$$
$$H_2 \xrightarrow{\text{Ib}} \begin{cases} H(a) \\ H(a) \end{cases} \cdots\cdots\cdots\cdots\cdots\cdots$$

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*) Department of Chemistry, Faculty of Science, Hokkaido University.
**) In the present paper protium or deuterium is denoted by P or D respectively; hydrogen is used as a generic term for protium and deuterium and H as a generic notation for P and D. Ethylene and ethane refer to mixtures of different deuterosubstituted ethylenes and those of such ethanes respectively.

where (a) denotes the adsorbed state and Ia *etc.* signify the respective elementary steps.

The present work is concerned with the elucidation of the above gap between the experimental suggestion and the theoretical inference. The detailed theoretical investigation was first conducted on the basis of the associative mechanism on the catalyzed interaction between P_2, C_2P_4 and C_2D_6 each of 10 mmHg initial partial pressure with special reference to the migration of deuterium atoms between the species. The migration was now observed with a mixture of P_2, C_2P_4 and ethane-d (approximately of 30% D content) each of about 10 mmHg initial partial pressure in order to check the theoretical conclusion.

Theoretical

Theory of the associative mechanism is developed below with the following notations:

E, A, H; ethylene, ethane, hydrogen.

P^E, P^A, P^H; partial pressures of E, A, H.

$v_+(\text{Ia})$, $v_+(\text{Ib})$, $v_+(\text{II})$, $v_+(\text{III})$: forward rates of steps Ia, Ib, II, III.

$v_-(\text{Ia})$, $v_-(\text{Ib})$, $v_-(\text{II})$, $v_-(\text{III})$: backward rates of steps Ia, Ib, II, III.

$\mathfrak{R}(\text{Ia})$ *etc.*: forward rates of step Ia *etc.* which would be the case in equilibrium of all steps of the associative mechanism but step Ia *etc.* respectively.

p^E, p^A, p^H, $p^{C_2H_4(a)}$, $p^{H(a)}$, $p^{C_2H_5(a)}$: BOLTZMANN factors of the chemical potentials μ^E, μ^A, μ^H, $\mu^{C_2H_4(a)}$, $\mu^{H(a)}$, $\mu^{C_2H_5(a)}$ of E *etc.* respectively, *e.g.*

$$p^E = \exp(-\mu^E/RT),$$

where R is the gas constant.

$\gamma(C_2H_4)$, $\gamma(H)$, $\gamma(C_2H_5)$: $\gamma(C_2H_4) = p^E/p^{C_2H_4(a)}$
$$\gamma(H) = (p^H)^{1/2}/p^{H(a)}$$
$$\gamma(C_2H_5) = p^E(p^H)^{1/2}/p^{C_2H_5(a)}$$

Γ: $\Gamma = P^A/K_p P^E P^H$, where K_p is the equilibrium constant of reaction $C_2H_4 + H_2 = C_2H_6$, *i.e.* $K_p = P_e^A/P_e^E P_e^H$, where suffix e signifies particular values in equilibrium of the reaction. The values of K_p are 1.56×10^{12} (50°), 2.11×10^9 (100°) and 1.32×10^7 mmHg^{-1} (150°C) as interpolated from the data given in LANDOLT "Tabellen" Erg. IIIc, p. 2622.

V: steady rate of reaction $C_2H_4 + H_2 = C_2H_6$, *i.e.* $V = dP^A/dt$.

The relations between the above quantities useful for the present theoreti-

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cal treatment are summarized below[*].

1. The steady state condition of the reaction is
$$V = v_+(\text{Ia}) - v_-(\text{Ia}) = v_+(\text{Ib}) - v_-(\text{Ib})$$
$$= v_+(\text{II}) - v_-(\text{II}) = v_+(\text{III}) - v_-(\text{III}). \tag{2.1}$$

2. It follows from the above definitions that
$$
\begin{aligned}
v_+(\text{Ia}) &= \Re(\text{Ia}) & v_-(\text{Ia}) &= \Re(\text{Ia})\,\gamma(\text{C}_2\text{H}_4)\\
v_+(\text{Ib}) &= \Re(\text{Ib}) & v_-(\text{Ib}) &= \Re(\text{Ib})\,\gamma(\text{H})^2\\
v_+(\text{II}) &= \Re(\text{II})\,\gamma(\text{H})\,\gamma(\text{C}_2\text{H}_4) & v_-(\text{II}) &= \Re(\text{II})\,\gamma(\text{C}_2\text{H}_5)\\
v_+(\text{III}) &= \Re(\text{III})\,\gamma(\text{H})\,\gamma(\text{C}_2\text{H}_5) & v_-(\text{III}) &= \Gamma\Re(\text{III})
\end{aligned} \tag{2.2}
$$

3. $\Re(\text{Ia})$ etc. were estimated as follows[4)6] with reference to experimental results[8)9]:
$$\Re(\text{Ia}) \gg \Re(\text{Ib}),\ \Re(\text{II}),\ \Re(\text{III});\ \Re(\text{Ia}) \gg V \tag{2.3}$$
$$
\begin{aligned}
\Re(\text{Ib})^{[**]} &= 2.0573 \times 10^{-18} \times 10^{\frac{-1356.6}{T}} \times P^H (P^E)^{0.525} \rho\\
\Re(\text{II}) &= 2.4687 \times 10^{-20} \times 10^{\frac{-220.12}{T}} \times (P^H)^{1/2} P^E \rho\\
\Re(\text{III}) &= 2.4012 \times 10^{-25} \times 10^{\frac{1092.3}{T}} \times P^H P^E \rho
\end{aligned} \tag{2.4}
$$
where ρ is a common factor.

4. Eq. (2.1) is developed on substitution of $v_+(\text{Ia})$ etc. from (2.2) as
$$V = \Re(\text{Ia})(1 - \gamma(\text{C}_2\text{H}_4)) = \Re(\text{Ib})(1 - \gamma(\text{H})^2)$$
$$= \Re(\text{II})(\gamma(\text{H})\,\gamma(\text{C}_2\text{H}_4) - \gamma(\text{C}_2\text{H}_5))$$
$$= \Re(\text{III})(\gamma(\text{H})\,\gamma(\text{C}_2\text{H}_5) - \Gamma). \tag{2.5}$$

5. We have from (2.3) and the first equation of (2.5)
$$\gamma(\text{C}_2\text{H}_4) \fallingdotseq 1 \tag{2.6}$$

6. Eq. (2.5) is now written with reference to (2.6) as
$$V = \Re(\text{Ib})(1 - \gamma(\text{H})^2) = \Re(\text{II})(\gamma(\text{H}) - \gamma(\text{C}_2\text{H}_5))$$
$$= \Re(\text{III})(\gamma(\text{H})\,\gamma(\text{C}_2\text{H}_5) - \Gamma). \tag{2.7}$$

The rate of migration of hydrogen atoms in ethane into hydrogen or ethylene is now determined relative to the steady rate V as follows. The values of $v_+(\text{s})$'s and $v_-(\text{s})$'s are determined with given conditions of temperature and partial pressures of the reaction partners by substituting $\Re(\text{Ia})$ etc. from (2.4) into (2.7), and solving the two simultaneous equations thus obtained

[*] cf. Refs. 3) and 4) as to the detailed presentation.
[**] Experimental results have required the revision of this equation[7]. An approximate calculation with the revised equation have shown that the revision made little difference.

for $\gamma(H)$ and $\gamma(C_2H_5)$; the values of $\gamma(H)$ and $\gamma(C_2H_5)$ thus obtained and those of $\Re(s)$'s given by (2.2) determine in turn those of $v_+(s)$'s and $v_-(s)$'s and in consequence the value of V by (2.7) except a common factor ρ, which cancels out in the ratios $v_+(s)/V$ and $v_-(s)/V$. Tab. 1 shows the values of various quantities thus calculated for the catalyzed interaction of H_2, C_2H_4 and C_2H_6 each of 10 mmHg initial partial pressure.

It is now necessary for the migration that C_2D_6 causes the reversal of step III, if not sufficient. Hence we calculate the upper limit of the amount of deuterium in ethane, which migrates until 10 mmHg ethylene in the above mixture decreases to 1 mmHg by the catalyzed hydrogenation. Denoting the amount of the ethane molecules involved in the reversal of step III by P^{Am} mmHg we have

$$\frac{v_-(III)}{V} = \frac{dP^{Am}}{dt} \bigg/ \frac{dP^A}{dt}$$

or

$$dP^{Am} = \frac{v_-(III)}{V} dP^A .$$

P^{Am} is hence integrated diagrammatically using $v_-(III)/V$ given in Tab. 1 as a function of P^A with initial condition $P^{Am}=0$ at $P^A=10$ mmHg, as

Temp. °C	P^{Am} mmHg
50	8.1×10^{-11}
100	1.2×10^{-8}
150	1.4×10^{-6}

Let now the destination of deuterium atoms from C_2D_6 be hydrogen, ethylene or ethane respectively exclusively; in the last case each deuterium atom of the above origin forms C_2P_5D being combined with P_2 and C_2P_4. The atomic percent of deuterium in hydrogen or ethylene and the mole percent of C_2P_5D in ethane are hence calculated as below noting that the gas mixture consists, at the end of the experiment supposed above, of 1 mmHg hydrogen, 1 mmHg ethylene and 19 mmHg ethane.

Temp. °C	Atomic percent of deuterium in		Mole percent of C_2P_5D in ethane
	hydrogen	ethylene	
50	2.4×10^{-8}	1.2×10^{-8}	2.7×10^{-8}
100	3.6×10^{-6}	1.8×10^{-6}	4.0×10^{-5}
150	4.2×10^{-4}	2.1×10^{-4}	4.7×10^{-3}

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TABLE 1. Theoretical data on the catalyzed hydrogenation

$$P^H = P^E = P^A = 10 \text{ mmHg}$$

| React. temp. (°C) | Partial pressure (mmHg) | | | $r\,(\text{H})$ | $r\,(\text{C}_2\text{H}_5)$ | $\dfrac{V}{V_0}$ *) | $\dfrac{v_+(\text{Ib})}{V_0}$ | $\dfrac{v_-(\text{Ib})}{V_0}$ |
	P^H	P^E	P^A					
50	10	10	10	0.2734	0.2565	1	1.0808	0.0808
	8	8	12	0.2865	0.2699	0.705	0.770	0.065
	6	6	14	0.3044	0.2881	0.451	0.497	00.46
	4	4	16	0.3310	0.3152	0.238	0.268	00.30
	2	2	18	0.3817	0.3667	0.0798	0.090	0.0102
	1	1	19	0.4353	0.4214	0.0264	0.0324	0.0060
100	10	10	10	0.6720	0.6409	1	1.824	0.824
	8	8	12	0.6907	0.6612	0.671	1.30	0.629
	6	6	14	0.7143	0.6868	0.405	0.837	0.432
	4	4	16	0.7461	0.7215	0.197	0.452	0.255
	2	2	18	0.7961	0.7761	0.0567	0.1567	0.100
	1	1	19	0.8396	0.8238	0.0159	0.0545	0.0386
150	10	10	10	0.9098	0.8866	1	5.81	4.81
	8	8	12	0.9176	0.8964	0.653	4.14	3.487
	6	6	14	0.9269	0.9080	0.376	2.67	2.294
	4	4	16	0.9383	0.9225	0.172	1.44	1.268
	2	2	18	0.9543	0.9426	0.0446	0.499	0.4544
	1	1	19	0.9663	0.9579	0.0115	0.174	0.1625

*) V_0 is the value of V at $P^H = P^E = P^A = 10$ mmHg.

The atomic or mole percents given in the above Table are upper limits in the respective cases because the reversal of III is not sufficient for arriving at any of the destinations, the destination is not in general exclusive in the above sense and ethane is no more pure C_2D_6 at the end of the experiment. The sensitivity of the mass spectrometer is around 10^{-2} mole%, so that the migration of D atoms in question should completely escape the mass spectrometric detection.

Experimental

1. Materials

The C_2P_4, C_2P_6, P_2 and D_2 used were supplied by TAKACHIHO Chemical Co., Ltd., Tokyo, the purities guaranteed by the supplier being 99.8% for the first two, 99.99% for the third and 99.7% for the last, which were mass

$C_2H_4 + H_2 = C_2H_6$ in the presence of nickel

$\dfrac{v_+(\text{II})}{V_0}$	$\dfrac{v_-(\text{II})}{V_0}$	$\dfrac{v_+(\text{III})}{V_0}$	$\dfrac{v_-(\text{III})}{V_0}$	$\dfrac{v_-(\text{III})}{V}$	$\dfrac{v_+(\text{Ia})}{V_0}$	$\dfrac{v_-(\text{Ia})}{V_0}$
16.23	15.23	1	9.14×10^{-13}	9.14×10^{-13}	∞	∞
12.15	11.45	0.705	1.096×10^{-12}	1.55×10^{-12}	"	"
8.42	7.97	0.451	$1.28 \times$ "	$2.84 \times$ "	"	"
4.97	4.73	0.238	$1.46 \times$ "	$6.14 \times$ "	"	"
2.03	1.95	0.0798	$1.65 \times$ "	2.07×10^{-11}	"	"
0.816	0.79	0.0264	$1.735 \times$ "	$6.57 \times$ "	"	"
21.6	20.6	1	1.084×10^{-10}	1.084×10^{-10}	"	"
15.9	15.2	0.671	$1.30 \times$ "	$1.94 \times$ "	"	"
10.7	10.3	0.405	$1.52 \times$ "	$3.76 \times$ "	"	"
6.07	5.87	0.197	$1.73 \times$ "	$8.79 \times$ "	"	"
2.29	2.23	0.0567	$1.95 \times$ "	3.44×10^{-9}	"	"
0.855	0.84	0.0159	$2.06 \times$ "	1.29×10^{-8}	"	"
39.1	38.1	1	9.41×10^{-9}	9.41×10^{-9}	"	"
28.2	27.5	0.653	1.09×10^{-8}	1.26×10^{-8}	"	"
18.5	18.1	0.376	$1.147 \times$ "	$3.05 \times$ "	"	"
10.2	10.0	0.172	$1.51 \times$ "	$8.79 \times$ "	"	"
3.66	3.62	0.0446	$1.69 \times$ "	3.79×10^{-7}	"	"
1.32	1.31	0.0115	$1.79 \times$ "	1.56×10^{-6}	"	"

spectroscopically confirmed by the present authors.

Nickel catalyst was nickel wire of 0.1 mm diameter supplied by TANAKA Noble Metal Co., Ltd., Tokyo, of 99.9% purity as guaranteed by the supplier and confirmed by Dr. M. NISHIMURA of Chemistry Department, Faculty of Science, Hokkaido University.

2. Apparatus

The apparatus used is shown in Fig. 1. The arrows indicate the direction and the course of circulation of the reacting gas mixture. The volume of the circulation system was about 300 cc. CP is the pump, which circulates the gas mixture with the rate adjusted to such value as the circulation is completed once every 30 sec. which is adequate to keep the composition in the circulation system homogeneous throughout. The rate of circulation was measured by

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circulating a mixture of ethylene and hydrogen, immersing trap T_2 into liquid nitrogen and measuring the rate of pressure decrease by condensation of ethylene by manometer M_1. The circulation pump was of usual type operated by a piston with an iron piece sealed in, solenoids and four ground-fit valves, but improved in the following respects; twelve pieces of solenoids placed around the cylinder as shown in Fig. 1 were excited successively to pull the piston up and down smoothly and the four valves were operated magnetically for certainty by solenoids placed outside. This improvement made the fluctuation of reading of manometer M_1 hardly visible and the same was the case with silicon oil manometer M_4 which bridged over the in- and out-let of the reaction vessel.
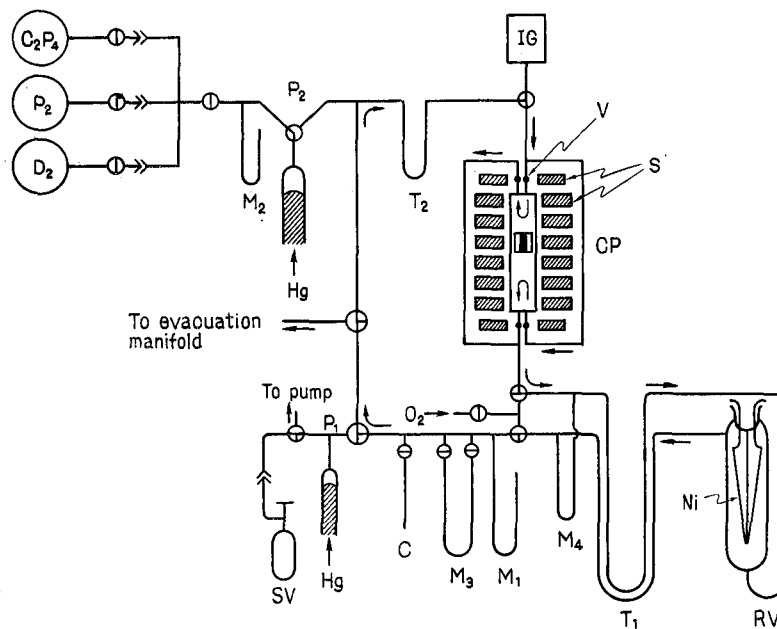

Fig. 1. Apparatus.
C : capillary tube, CP : circulation pump, IG : ionization gauge, M_1, M_2 : mercury manometer, M_3, M_4 : silicon oil manometer, P_1, P_2 : gas pipette, RV : reaction vessel, S : solenoid, SV : sampling vessel, T_1, T_2 : trap, V : valve.

Pipette P_1 was used to sample constantly a definite amount *ca.* 3 cc of the reacting gas for mass spectrometric analyses. Pipette P_2 was of volume adjustable by means of mercury from zero to 100 cc, which served to introduce a known amount of gas into the circulation system being provided with mercury manometer M_2.

RV is the reaction vessel, in which nickel wire of 30 cm length and 0.1 mm diameter was sealed; the nickel wire was inserted in a Wheatstone bridge as its one arm so that the wire could be heated electrically and its temperature measured. Trap T_1 was immersed in dry ice in order to protect the wire against poisoning of mercury, silicon oil and tap grease vapors. The inner surface of trap T_1 was rugged to ensure the condensation of the vapor. Mercury manometer M_1 and silicon oil manometer M_3 measured the pressure inside the circulation system, the latter operating as a differential pressure gauge with one of its arms shut off from the circulation system.

3. Procedure

3. 1. Activation of the catalyst

The nickel wire in the reaction vessel was activated as follows by repeated oxidation at 600°C followed by reduction at 300°C. The circulation system was evacuated with the reaction vessel placed in an electric furnace at 300°C, trap T_1 then immersed in dry ice and oxygen of about 200 mmHg introduced into the circulation system. The wire was heated by electric current through the bridge at 400°C for 10 min., then at 500°C for 10 min. and finally at 600°C for 1 hr. Residual oxygen was now evacuated, hydrogen of about 30 mmHg introduced and the oxidized wire thus reduced at 300°C for 2 hrs. operating the circulation pump meanwhile. The above procedure was repeated once more similarly except that the reduction continued for about 20 hrs.

3. 2. Preparation of deuterated ethane

The deuterated ethane was prepared as follows by allowing C_2P_4 to react with deuterium on the nickel wire activated as described above.

The reaction vessel was immersed in ice water, the circulation pump put in operation and deuterium of about 10 mmHg and subsequently C_2P_4 of about 10 mmHg were introduced into the circulation system. The reaction vessel was now immersed in an oil bath at 100°C thus allowing the deuteration to proceed to convert half of the ethylene into ethane. After having been stripped of the ethylene and ethane by immersing trap T_2 in liquid nitrogen, the residual hydrogen was evacuated and a fresh charge of deuterium of about 10 mmHg replaced. The fresh charge of deuterium was mixed with the ethylene and ethane just now condensed by removing the liquid nitrogen and the deuteration was allowed to proceed similarly but now to completion. After having been stripped of the deuterated ethane similarly, the residual hydrogen was evacuated, the deuterated ethane transferred to capillary tube C immersed in liquid nitrogen. The deuterated ethane thus prepared will be referred to as ethane-d in what follows.

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3. 3. Reaction

P_2 and C_2P_4 each of 10 mmHg and then ethane-d of 9 mmHg were successively introduced into the circulation system with the reaction vessel immersed in ice water, circulated for 2 hrs. and then sampled, which is signified as run 1. The ice water was now replaced with an oil bath at 100°C to allow the reaction to proceed until the pressure had decreased by a pre-determined value. The resultant gas was subjected to the further similar runs successively at 50 and then at 150°C, the series of runs at 100, 50 and 150°C was repeated three times in the same order and then run 11 was conducted at 100°C; runs from 1 to 11 were thus carried out with a single charge of reacting gas. Pressure was recorded from time to time during every run and the reacting gas was sampled at the end of every run by a constant volume about 3 cc for mass spectrometric analysis.

3. 4. Analysis by mass spectrometer

The sampling vessel SV containing the reacting mixture was immersed in liquid nitrogen to separate the hydrogen from the hydrocarbon mixture and

TABLE 2. Experimental results

Run no.	Total pressure[a] (mmHg)		React. temp. (°C)	Approx. duration of reaction (min)	Approx. partial[d] pressure of hydrogen (calc.) (mmHg)
	Initial–Final	ΔP			
1	29.0[b]– 29.0	0	0	120	10 – 10
2	28.75 – 27.47	1.28	100	40	10 – 9
3	27.23 – 26.33	0.90	50	240	9 – 8
4	26.09 – 24.60	1.49	150	30	8 – 6.5
5	24.39 – 23.38	1.01	100	65	6.5 – 5.5
6	23.17 – 22.20	0.97	50	510	5.5 – 4.5
7	22.00 – 21.15	0.85	150	75	4.5 – 3.5
8	20.96 – 19.84	1.12	100	280	3.5 – 2.5
9	19.66 – 19.27	0.39	50	840	2.5 – 2.0
10	10.09 – 18.73	0.36	150	180	2.0 – 1.5
11	18.56 – 18.36[e]	0.20	100	220	1.5 – 1.2

a) 1. Pressure measured with the reaction vessel immersed in ice water.
     2. Total pressure decreased by 0.9% by the sampling after each run.
b) The reacting mixture consists of 10 mmHg P_2, 10 mmHg C_2P_4 and 9.0 mmHg ethane–d.
c) The reacting mixture consists of 1.26 mmHg hydrogen, 1.26 mmHg ethylene and 15.84 mmHg ethane as calculated from results of the foregoing runs.
d) This column is attached for convenience of comparing Tab. 2 with Tab. 1.

the hydrogen thus separated was introduced into the mass spectrometer RMU–6 supplied by HITACHI Works, Ltd., Tokyo. This method for separating hydrogen was preliminarily confirmed to be mass spectrometrically complete. The mixture of the hydrocarbons in the sampling vessel was then subjected to the mass spectrometric analyses. The ionization potential used in the analyses was 80 V.

Results

Tab. 2 shows the results of runs conducted as mentioned above with a single charge of reacting mixture. The activity of the catalyst was kept almost unchanged from run 2 to 11 throughout, as confirmed by nearly the same rate to that of run 2 as observed in a run conducted under the same condition to that of run 2 immediately after run 11 with a fresh charge of reacting mixture.

Tab. 3 shows the observed mass spectra of hydrogen and the mixture of hydrocarbons for the first (run 1) and the last run (run 11). It is evident from Tab. 3, that the quantity of C_2D_6 remained unchanged throughout until 9 out of 10 mmHg ethylene had been converted into ethane. C_2D_6, which has no higher deuterated precursor, ought to decrease under the conditions employed,

TABLE 3. Mass spectra of hydrogen and ethylene-
ethane mixture of Run 1 and Run 11[a]

Run no. m/e	1	11	
	obs.[b]	obs.[b]	corr.[c]
36 (C_2D_6)	6.1[d]	5.6[d]	6.1
35 (C_2PD_5)	10.1	9.3	10.1
34	18.1	16.6	18.1
33	26.7	24.5	26.7
32	90.8	83.6	91.2
4 (D_2)	0	0	
3 (PD)	0	0	

a) The sensitivity of the mass spectrometer used was ± 0.1 division.
b) The obs. values of one of the samples extracted from the reacting mixture by a constant volume *ca.* 3 cc in each sampling.
c) The value expected in the absence of extractions, which is calculated by multiplying the obs. values by $(1/1-0.009)^{10}$, where the figure 0.009 is the fraction of the mixture extracted per run and the exponent 10 is the number of times of foregoing extractions of run 11.
d) Number of divisions on the recording chart, one division being 2 mm long.

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should hydrogen atoms in ethane migrate. The invariant amount of C_2D_6 verifies in consequence unequivocally the absence of the migration in question.

The above conclusion is further established by the fulfilment of the necessary conditions of the absence of the migration, *i. e.*

(1) no emergence of deuterium into hydrogen

and

(2) constancy of the amounts of C_2PD_5, $C_2P_2D_4$, $\cdots$, $C_2P_4D_2$ in ethane-d, which are readily seen from Tab. 3. The experimental results thus verify the theoretical conclusion from the associative mechanism on the one hand and exclude any other mechanisms operative which effect the migration in question under the present experimental condition.

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