# Hydrogenation of Ethylene on Metal Electrodes

Part 5.—Reduction of Light Ethylene on Pt in Deuteroperchloric Acid Solution and the Dual-pathway Mechanism

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#### Received 5th January, 1981

Electroreduction of light ethylene on a platinum electrode was conducted in a heavy-water solution of deuteroperchloric acid. Deuterium-atom distributions in the product, ethane, support the previous conclusion that ethylene diffusion is rate-controlling at potentials less positive than *ca.* 100 mV, whereas the surface reaction is rate-controlling at more positive potentials where the Tafel line holds. The D-atom distribution in the latter potential region reveals double maxima at  $[^{2}H_{a}]$ - and  $[^{2}H_{6}]$ -ethanes. This distribution is explained by the dual-pathway mechanism which assumes two reaction rates for the step

$$C_2H_4(a) + H(a) \rightleftharpoons C_2H_5(a).$$

The difference in the reaction rate will be attributed to the difference in the adsorption state of  $C_2H_4(a)$  but not of H(a), since only the weakly adsorbed hydrogen atoms are active in the hydrogenation.

Reduction of light ethylene with  $D_2$  on platinum in deuteroperchloric acid solution gives the same results. A computer simulation based on the above mechanism can reproduce quantitatively not only the present distributions but also others given in the literature, even those observed for the gas-phase heterogeneous reduction.

The reduction of ethylene on platinum in aqueous acid solution has been studied by two methods; one is the reduction with hydrogen gas on open-circuit<sup>1-3</sup> and the other is by electroreduction without hydrogen.<sup>4</sup> These methods have shown that the surface process is controlled by the elementary step

$$C_2H_5(a) + H(a) \rightarrow C_2H_6$$

of the Horiuti–Polanyi mechanism, where (a) denotes the adsorbed state.

The isotopic tracer method is often a powerful tool for the elucidation of reaction mechanisms and has been widely used in heterogeneous catalyses in gas phase.<sup>5</sup> In the electrochemical system, Langer *et al.*<sup>6</sup> performed the electrogenerative hydrogenation of ethylene in DClO<sub>4</sub> + D<sub>2</sub>O solution using a Pt fuel-cell electrode. They showed an interesting D-atom distribution in the ethane produced but no detailed mechanistic analysis was attempted. We conducted the reduction of C<sub>2</sub>H<sub>4</sub> with D<sub>2</sub> in HClO<sub>4</sub> + H<sub>2</sub>O solution and concluded that there is a rapid occurrence of

$$C_2H_4(a) + H(a) \rightleftharpoons C_2H_5(a)$$

back and forth at a much larger rate than that of the following step

$$C_2H_5(a) + H(a) \rightarrow C_2H_6$$

In the present study the reduction of  $C_2H_4$  was carried out with or without  $D_2$  (open-circuit or electroreduction) in  $DClO_4 + D_2O$  solution so that the deuterium fraction of the adsorbed hydrogen atoms was always kept close to that of the solution during the reaction. This is one of the advantages which the electrochemical system provides.

The results offer new information on the reduction mechanism which also applies to heterogeneous reduction in the gas phase. The origin of the present dual-pathway mechanism is discussed.

# EXPERIMENTAL

The apparatus, materials and procedure used have been described in previous papers.<sup>1-3</sup> The present electrolytic solution was prepared by dissolving  $DClO_4$  (> 99% D, Merck) into purified  $D_2O$  at a concentration of 0.9 mol dm<sup>-3</sup>. The final deuterium fraction of the solution after a series of experiments was determined as 0.88 by nuclear magnetic resonance spectroscopy. Ethane has been confirmed as the only product by gas-chromatographic analysis.<sup>4</sup>

# RESULTS

#### DEUTERIUM-ATOM DISTRIBUTIONS IN ETHANE FROM ELECTROREDUCTION

The previous measurements reveal three regions on the Tafel plot:<sup>4</sup> a linear Tafel relation region (fig. 1, solid curve A), a diffusion region of ethylene (B) and a hydrogen evolution region (C), respectively. Potentiodynamic studies with a triangular pulse superimposed on a reduction potential show the following facts:<sup>4</sup> (1) over the Tafel region, the surface is almost saturated with adsorbed species from ethylene and (2) in both the regions of ethylene diffusion and hydrogen evolution the surface is almost covered with adsorbed hydrogen atoms.



FIG. 1.—Tafel plot of the reduction current (above) and D-atom distributions in ethane (below). Above: 0.9 mol dm<sup>-3</sup> DClO<sub>4</sub>, solid curve,  $p(C_2H_4) = 10$  cmHg, dotted curve,  $p(C_2H_4) = 0$  cmHg (H<sub>2</sub> evolution). Below: (a) 80, (b) 160 mV.

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The present electroreduction of light ethylene in  $DClO_4 + D_2O$  solution gives the same Tafel plot but reveals potential-dependent D-atom distributions in ethane, as shown in fig. 1. The distribution (b) from region (B) shows a predominant production of  $[{}^{2}H_{2}]$ ethane. This supports the previous conclusion<sup>4</sup> that ethylene diffusion is rate-determining since the ethylene molecule once reaching the surface is immediately deuterated to ethane and desorbs. Also noted is the production of heavier deuteroisomers than  $[{}^{2}H_{2}]$ ethane, although their amounts are small. This fact suggests an occurrence of rapid H/D exchange on the surface.

The distribution (a) from region (A) clearly reveals double maxima for  $[{}^{2}H_{2}]$ - and  $[{}^{2}H_{6}]$ -ethanes. Although the hydrogenation of ethylene has been extensively studied on many catalysts in the gas phase,<sup>7</sup> such a distribution seems not to have been reported in the literature.

notential	time				current t = 20 min	D- fraction				
/mV	/min	$[{}^{2}H_{0}]$	[ <sup>2</sup> H <sub>1</sub> ]	[ <sup>2</sup> H <sub>2</sub> ]	[ <sup>2</sup> H <sub>3</sub> ]	[ <sup>2</sup> H <sub>4</sub> ]	[ <sup>2</sup> H <sub>5</sub> ]	[ <sup>2</sup> H <sub>6</sub> ]	/mA	ethane
160	20	0.0	10.9	40.2	7.4	6.2	13.4	21.9	2.70	
	40	0.0	12.2	36.9	7.6	7.8	13.8	21.6		
	60	0.0	13.6	32.2	6.0	8.9	15.9	23.3		and a Manatana
	average	0.0	12.2	36.4	7.0	7.6	14.4	22.3		0.570
170	20	0.0	5.6	36.4	8.3	9.7	15.0	25.0	1.71	
	40	0.0	11.8	34.7	6.3	8.1	14.1	25.0		
	60	0.0	3.4	38.1	8.7	10.0	15.9	23.9		
	average	0.0	6.9	36.4	7.8	9.3	15.0	24.6		0.605
200	20	0.0	0.0	42.9	5.5	6.0	14.8	30.7	0.179	
	40	0.0	5.4	35.2	7.0	9.2	14.5	28.9		
	60	0.0	4.6	40.2	7.0	8.1	13.7	26.5		
	average	0.0	3.3	39.4	6.5	7.8	14.3	28.7		0.628
230	20	0.0	0.0	41.7	4.6	7.6	12.2	33.9	0.010	
	40	0.0	0.0	47.1	6.3	7.7	10.7	28.2		
	60	0.0	7.6	41.0	5.9	6.0	11.2	28.3		
	average	0.0	2.5	43.3	5.6	7.1	11.4	30.1	_	0.620
ave	erage in th	e								
Т	afel region	0.0	6.2	38.9	6.7	8.0	13.8	26.4		0.606

TABLE 1.—D-ATOM DISTRIBUTIONS I	N ETHANE	PRODUCED	BY	ELECTROREDUCTI	ON A'	T VARIOUS
	POTE	INTIALS				

Table 1 shows D-atom distributions of ethane obtained by the electroreduction at various potentials and reaction times in the Tafel region ( $\phi > 100 \text{ mV}$ ). The distributions are safely taken to be independent of the reaction time at each potential studied. Their change with potential is only slight and very small when compared with that of the reaction current, *i.e.* the latter at 160 mV reduces to several thousandths at 230 mV. Thus, those distributions are taken to be essentially the same irrespective of the potential in the Tafel region. Accordingly, the reaction mechanism will stay unchanged.

A basic problem arises as to whether the pathway of H/D exchange is included in the reduction pathway or not. To answer the above problem we carried out the following measurement.

		current $t = 20$ min		$[{}^{2}\mathrm{H}_{i}]$ ethane (%)								
run	ın	$r = 20 \text{ mm}^{-1}$	[ <sup>2</sup> H <sub>0</sub> ]	$[{}^{2}H_{1}]$	$[{}^{2}H_{2}]$	[ <sup>2</sup> H <sub>3</sub> ]	$[{}^{2}H_{4}]$	$[{}^{2}H_{5}]$	$[{}^{2}H_{6}]$	ethane		
1	200 mV, 2 min; open, 3 min;	0.175	0.0	2.2	37.6	6.6	7.2	15.1	31.4	0.650		
2	10 times	0.179	0.0	0.0	42.9	5.5	6.0	14.8	30.7	0.641		

TABLE 2.—EFFECT OF THE INTERRUPTION OF THE ELECTROREDUCTION ON THE D-ATOM DISTRIBUTION

The reduction at 0.20 V was continued for 2 min and then interrupted by opening the electric circuit for 3 min (run 1, table 2). This scheme was repeated ten times. The amount of adsorbed hydrogen on open circuit is much less than at 0.2 V because of the consumption of the adsorbed hydrogen atoms by ethylene. In this case the potential shifts gradually in the positive direction. The D-atom distribution thus obtained is in close agreement with that from the continuous reduction (run 2). Another experiment where the electrode was polarized in the presence of  $C_2H_4$  at 0.25 V for 20 min in advance of the reduction at 0.2 V, shows no increase in the H/D exchange. At 0.25 V the amount of the adsorbed hydrogen decreases to a considerable extent and the reduction current becomes negligible. These results clearly confirm the absence of H/D exchange over the interruption periods and hence that H/D exchange occurs when the reduction proceeds.

Table 3.—Absence of H/D exchange during the contact of  $C_2H_6$  with Pt in 0.9 mol  $dm^{-3}\ DClO_4 + D_2O$  solution

	notential	time	[ <sup>2</sup> H <sub>i</sub> ]ethane	[ <sub>i</sub> ]ethane	: (%)				
run	/mV	/min	[ <sup>2</sup> H <sub>0</sub> ]	[ <sup>2</sup> H <sub>1</sub> ]	$[{}^{2}H_{2}]$	$[{}^{2}H_{3}]$	$[{}^{2}H_{4}]$	$[{}^{2}H_{5}]$	[ <sup>2</sup> H <sub>6</sub> ]
1 2	180 180	40 40	99.2 99.2	0.16 0.00	0.20 0.33	0.05 0.05	0.00 0.03	0.10 0.03	0.34 0.30

The H/D exchange between light ethane and  $DClO_4 + D_2O$  solution was tested. The results in table 3 deny the exchange within experimental error.

# DEUTERIUM-ATOM DISTRIBUTIONS FROM OPEN-CIRCUIT REDUCTION AND A COMPARISON WITH THOSE FROM ELECTROREDUCTION

The results obtained from  $C_2H_4 + D_2$  in HClO<sub>4</sub> solution on open circuit have been reported elsewhere.<sup>3</sup> The D-atom distributions of ethane from  $C_2H_4 + D_2$  in DClO<sub>4</sub> + D<sub>2</sub>O solution or  $C_2H_4 + H_2$  in DClO<sub>4</sub> + D<sub>2</sub>O solution are summarized in table 4, where runs 2, 3 and 5 are under the conditions of diffusion control of D<sub>2</sub>, H<sub>2</sub> and  $C_2H_4$ , respectively [ref. (1)]. To compare these distributions with those from the electroreduction on the same electrode, runs 1 and 4 were supplemented in the Tafel region and the diffusion region of ethylene, respectively.

First, it is seen from runs 1 and 2 conducted at similar conditions of potential and ethylene pressure that the D-atom distributions of ethane are similar to each other, irrespective of the methods of the reduction. This fact indicates that a mechanism for

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TABLE 4.—COMPARISON OF THE D	-ATOM DISTRIBUTIONS	OBTAINED BY TH	HE OPEN-CIRCUIT	REDUCTION
AND BY EI	lectroreduction (0.9	9 mol dm <sup>-3</sup> DC	lO <sub>1</sub> )	

		ini	itial									_ <b>.</b>
		pressure/ cmHg		tima	$[{}^{2}\mathbf{H}_{i}]$ ethane (%)							
run	i -	$C_2H_4$	$H_2/D_2$	/min	[ <sup>2</sup> H <sub>0</sub> ]	$[{}^{2}H_{1}]$	$[{}^{2}H_{2}]$	$[{}^{2}H_{3}]$	$[{}^{2}H_{4}]$	$[{}^{2}H_{5}]$	$[{}^{2}H_{6}]$	ethane
1	electro-	11.80	0	20	0.0	7.6	39.6	8.6	5.1	14.3	24.9	
	reduction,			40	0.0	13.6	31.8	8.9	5.9	15.1	24.6	_
	190 mV			60	0.0	9.1	38.7	9.1	6.6	14.4	22.2	
				average	0.0	10.1	36.7	8.9	5.9	14.6	23.9	0.584
2	open-	12.30	D,	20	0.0	0.0	44.5	8.3	7.3	15.3	24.5	
	circuit		3.98	40	0.0	11.1	37.4	9.5	7.5	13.9	20.5	
	(180 mV			60	0.0	17.0	30.9	10.1	8.1	14.4	19.5	
	at 5 min)		-	average	0.0	9.4	37.6	9.3	7.6	14.5	21.5	0.574
3	open-	11.60	Н,	40	0.0	20.3	32.5	10.7	11.7	13.9	10.9	
	circuit		3.84	60	0.0	24.1	28.6	12.1	11.3	13.6	10.3	
	(180 mV at 5 min)		—	average	0.0	22.2	30.6	11.4	11.5	13.8	10.6	0.494
4	electro-	1.31	0	20	0.0	18.1	41.9	15.4	10.5	7.1	7.0	
	reduction,			40	0.0	15.4	54.3	15.2	10.5	6.7	6.8	
	80 mV			60	0.0	19.5	42.3	15.2	8.7	7.1	9.1	
			_	average	0.0	17.7	43.2	15.3	9.9	7.0	7.6	0.450
5	open-	1.82	H.	20	1.9	12.8	58.1	13.2	6.7	3.6	3.7	
	circuit		8.38	40	5.9	14.5	54.0	12.7	6.2	3.4	3.4	
	(70 mV, constant)			average	3.9	13.7	56.1	13.0	6.5	3.5	3.6	0.383

the H/D exchange is common to both the cases of electroreduction and open-circuit reduction.

Secondly, a comparison of runs 2 and 3 shows some difference in the  $[{}^{2}H_{1}]$ ,  $[{}^{2}H_{6}]$ and D-fraction in ethane. It is emphasized that although H<sub>2</sub> is used in run 3, the ethane produced shows a considerably high D-fraction in ethane. Light hydrogen atoms from the gaseous hydrogen incorporate only partly with the adsorbed ethylene. The remaining hydrogen atoms dissolve into the solution *via* rapid exchange through the step

$$H^+ + e^- \rightleftharpoons H(a).$$

Runs 4 and 5 lead to the same conclusion as runs 1 and 2, although the D-atom distributions differ because  $H_2$  was used in run 5.

# DISCUSSION

It has been deduced<sup>1-4</sup> that the reduction of ethylene on a platinum electrode in acidic solution occurs by the following mechanism

$$\begin{array}{c}
C_{2}H_{4}(b) \underbrace{\leftarrow}_{(Ia)} C_{2}H_{4}(s) \underbrace{\leftarrow}_{(IIa)} C_{2}H_{4}(a) \\
H_{2}(b) \underbrace{\leftarrow}_{(Ib)} H_{2}(s) \underbrace{\leftarrow}_{(IIb)} \begin{cases} H(a) \\ H(a) \\ H(a) \\ H(a) \\ - - - - - - - - \end{cases} \underbrace{\leftarrow}_{(IV)} C_{2}H_{6} \tag{1}$$

where (Ia) and (Ib) denote the diffusion steps of ethylene and hydrogen, respectively, (IIa) and (IIb) represent the adsorption steps of these species, and (b), (s) and (a) specify the states of the designated species, *i.e.* in bulk solution, near the surface and in the adsorption layer, respectively.

In the above scheme, step (II *a*) has been concluded to be an irreversible molecular process<sup>3</sup> since no deuterium atoms are taken up into the ethylene reactant when  $C_2H_4$  is reduced with  $D_2$  in HClO<sub>4</sub> solution and no self-hydrogenation takes place when  $C_2H_4$  is brought into contact with a platinum electrode in HClO<sub>4</sub> solution.

Ethane also showed no H/D exchange with the adsorbed deuterium atoms from  $DClO_4 + D_2O$  solution even at potentials where ethylene is reduced (table 3). Ethane, once produced from ethylene, therefore does not readsorb on the surface in a dissociative manner, *i.e.* step (IV) in the above scheme is irreversible, in agreement with previous conclusion.<sup>1</sup>

Langer *et al.*<sup>6</sup> have discussed the H/D exchange through various steps, *i.e.* step (III) of scheme (1) and the following steps

$$2C_2H_5(a) \leftrightarrow C_2H_4(a) + C_2H_6 \tag{2}$$

$$C_2D_4(a) + C_2H_5(a) \xrightarrow{} C_2D_3H(a) + C_2H_4D(a)$$
(3)

$$C_2H_4(a) + D^+ + e^- \leftarrow C_2H_4D(a).$$
(4)

A common feature among steps (2)-(4) is that no adsorbed hydrogen atoms are involved. Therefore, if any of these processes occurs on the surface, the H/D exchange may proceed even under the conditions of no adsorbed hydrogen atoms. This is not the case as described earlier (table 2).

Moreover, surface coverages of  $C_2H_4(a)$  and  $C_2H_5(a)$  on the platinum under working conditions will in general be expected to vary with potential and thus affect rates of steps (2)-(4), giving rise to a potential dependence of the D-atom distribution. Here again the observed distributions (table 1) are independent of potential, contrary to expectation. Hence, it is most plausible to assume that the H/D exchange during reduction occurs through step (III) of scheme (1).

It has been reported that ethylene adsorbs on a Pt electrode in the form of an acetylenic radical<sup>8</sup> or other dissociated species.<sup>9,10</sup> If a highly dissociated species is assumed to undergo H/D exchange on the surface, a similar D-atom distribution may be expected for the electroreduction of acetylene. Thus the latter reduction was examined on the same electrode as for the reduction of ethylene. The reaction does not occur at potentials where ethylene is reduced. The D-atom distributions in table 5 are obtained at -30 mV (RHE), which is more negative by *ca*. 0.2 V than that for ethylene reduction. Furthermore, the D-atom distribution of ethane in table 5 differs

Table 5.—D-atom distributions in ethylene and ethane produced by electroreduction of light acetylene (0.9 mol dm<sup>-3</sup> DClO<sub>4</sub>)

<i>p</i> (C H.)	[ <sup>2</sup> H <sub>i</sub> ]ethylene (%)					$[{}^{2}H_{i}]$ ethane (%)								
$p(\mathbb{C}_2\Pi_2)$ /cmHg	/mV	/min	$[^{2}H_{0}]$	[ <sup>2</sup> H <sub>1</sub> ]	$[{}^{2}H_{2}]$	[2H3]	$[{}^{2}H_{4}]$	$[{}^{2}H_{0}]$	$[{}^{2}H_{1}]$	$[{}^{2}H_{2}]$	[ <sup>2</sup> H <sub>3</sub> ]	[2H4]	[ <sup>2</sup> H <sub>5</sub> ]	[2H6
4.76	-30	20	3.8	23.4	66.3	5.1	1.4	0.0	4.2	21.4	22.3	41.7	8,4	2.3

strikingly from those in table 1. Therefore, it is concluded that an acetylenic radical, if it exists, is not involved in either the H/D exchange or the reduction on Pt under the present working conditions. We exclude the possibility of participation by acetylenic species in the following treatments.

# EXPLANATION OF THE DEUTERIUM-ATOM DISTRIBUTION IN ETHANE BASED ON SCHEME (1)

The rate of formation of  $[{}^{2}H_{i}]$  ethane  $(C_{2}H_{6-i}D_{i})$ ,  $v_{i}$ , is expressed as follows based on scheme (1):

$$v_i = v(IV)(y_{i-1}y_D + y_iy_H),$$
 (5)

where  $\vec{v}(IV)$  denotes the unidirectional forward rate of step (IV),  $y_{i-1}$  and  $y_i$  are molar fractions of adsorbed ethyl radicals which contain (i-1) and *i* deuterium atoms, and  $y_D$  and  $y_H$  are atomic fractions of H(a) and D(a), respectively. The backward rate of step (IV) is not taken into account in eqn (5) because of the irreversibility of step (IV). Thus, we have  $\vec{v}(IV) = v_s$ , (overall reaction rate at steady state). Then, eqn (5) is rewritten as

$$v_i/v_s = y_{i-1}y_D + y_iy_H.$$
 (6)

The molar fraction of  $[{}^{2}H_{i}]$  ethane in the product at a given time,  $A_{i}$ , is defined as

$$A_i = \int_0^t v_i \mathrm{d}t \Big/ \int_0^t v_\mathrm{s} \mathrm{d}t,\tag{7}$$

and is reduced to the following expression according to the time-independent D-atom distribution of ethane (table 1):

$$A_i = v_i / v_{\rm s}.\tag{8}$$

From eqn (6) and (8) one obtains

$$A_i = y_{i-1} y_{\rm D} + y_i y_{\rm H}.$$
 (9)

Eqn (9) is simplified at i = 0 as  $A_0 = y_0 y_H$  without the first term, while at i = 6 as  $A_6 = y_5 y_D$  without the second term, because of the restriction that we have six hydrogen atoms. Thus eqn (9) gives rise to seven simultaneous equations. Further, the following conditions must be satisfied:

$$\sum_{i=0}^{5} y_i = 1, \tag{10}$$

$$y_{\rm D} + y_{\rm H} = 1.$$
 (11)

Solution of the simultaneous equations from eqn (9)-(11) with the values of  $A_i$  given in tables 1, 4 and ref. (3), yields the values of  $y_i$  and  $y_H$  (or  $y_D$ ) shown in table 6.

species	quantity	i	table 1 170 mV	table 4 run 2	ref. (3)	
$C_{2}D_{i}H_{6-i}$	$A_i$ /fraction	0	0.000	0.000	0.482	
(product)	6.	1	0.069	0.094	0.260	
		2	0.364	0.376	0.150	
		3	0.078	0.093	0.060	observed
		4	0.093	0.076	0.030	
		5	0.150	0.145	0.012	
		6	0.246	0.215	0.000	
H(a)	$y_{\rm H}(=1-y_{\rm D})$	_	0.164	0.220	0.790	
$C_{v}D_{i}H_{5-i}$	$v_i$ /fraction	0	0.000	0.000	0.610	
(adsorbed)		1	0.421	0.455	0.167	calc.
		2	0.075	0.099	0.145	eqn (9)-
		3	0.094	0.066	0.037	(11)
		4	0.087	0.108	0.028	
		5	0.474	0.268	0.008 J	
$C_{2}D_{i}H_{4-i}$	$x_i$ /fraction	0	0.000	0.000	0.772	
(adsorbed)	.,	1	2.565	2.072	0.007	calc.
		2	-12.62	- 6.905	0.182	eqn (15)
		3	64.91	24.83	-0.002	2 . /
		4	-330.4	87.69	0.036	

TABLE 6.—CALCULATED D-ATOM DISTRIBUTIONS IN THE REACTION INTERMEDIATES

A material balance with respect to the reaction intermediate of  $C_2H_{5-i}D_i(a)$  under steady-state conditions is expressed as follows, based on scheme (1):

$$\vec{v}(\text{III})(x_{i-1}y_{\text{D}} + x_iy_{\text{H}}) = [\vec{v}(\text{III}) + \vec{v}(\text{IV})]y_i,$$
 (12)

where  $x_{i-1}$  and  $x_i$  denote molar fractions of the adsorbed ethylene containing i-1 and i deuterium atoms, respectively. The above equation is rewritten with the condition

 $v_{\rm s} = \vec{v}({\rm IV})$ 

and

$$v_{\rm s} = \vec{v}({\rm III}) - \vec{v}({\rm III}), \tag{13}$$

$$x_{i-1}y_{\rm D} + x_i y_{\rm H} = y_i.$$
(14)

The above equation and eqn (9) give

$$A_{i} = x_{i-2}y_{\rm D}^{2} + 2x_{i-1}y_{\rm H}y_{\rm D} + x_{i}y_{\rm H}^{2}.$$
(15)

Values of  $x_i$  which satisfy eqn (15) are calculated by using  $A_i$  and the above  $y_H$  (or  $y_D$ ) values. Results are listed in table 6. Some of the  $x_i$  turn out to be unsuccessfully negative or larger than unity and lose their physical meaning. Thus the D-atom distribution observed indicates the operation of a more complicated mechanism for the surface process.

# COMPUTER SIMULATION OF THE DEUTERIUM-ATOM DISTRIBUTION BASED ON THE DUAL-PATHWAY MECHANISM

Next we examine the following two possibilities.

(1) There exist two kinds of surface portions where the H/D exchange [step (III)]

occurs with different rates, e.g.  $\vec{v}_1(\text{III})$  and  $\vec{v}_2(\text{III})$ . In this case eqn (15) is rewritten as

$$A_{i} = \sum_{j=1}^{2} c_{j} A_{ji} = \sum_{j=1}^{2} c_{j} (x_{i-2} y_{\rm D}^{2} + 2x_{i-1} y_{\rm D} y_{\rm H} + x_{i} y_{\rm H}^{2})_{j},$$
(16)

where  $A_{ji}$  is the portion of  $A_i$  which is yielded from the *j*th pathway with  $\vec{v}_j$ (III) and  $\vec{v}_i$ (III) and  $c_i$  is the weight of the *j*th pathway.

(2) There are two kinds of surface portions where step (V) occurs with different rates,  $\vec{v}_1(V)$  and  $\vec{v}_2(V)$ , generating different  $y_D$  values. In this case, we have the same form as eqn (16) but j refers to  $y_D(y_H)$ .

From these hypotheses, one can expect qualitatively that, with the conditions  $\vec{v}_1(\text{III}) < \vec{v}_2(\text{III})$  or  $\vec{v}_1(\text{V}) < \vec{v}_2(\text{V})$ ,  $A_{1i}$  will have a distribution with a peak at smaller  $[{}^2\text{H}_i]$  ethane values while the remaining distribution,  $A_{2i}$ , will show a peak at higher  $[{}^2\text{H}_i]$  ethane values, because the higher value of  $\vec{v}_2(\text{III})$  or  $\vec{v}_2(\text{V})$  tends to promote the H/D exchange.

In the preceding section, the observed  $A_i$  value was used to search D-atom distributions of the reaction intermediates on the surface but in this section we attempt to reproduce  $A_i$  by the following procedure.

First, a material balance of the adsorbed ethylene of  $C_2H_{4-i}D_i(a)$  under steady-state conditions is formulated by taking into account the irreversibility of step (II *a*) as follows:

$$X_i \vec{v}(\mathrm{II}\,a) = x_i \vec{v}(\mathrm{III}) - (P_i y_i + Q_i y_{i+1}) \vec{v}(\mathrm{III})$$
(17)

where  $X_i$  denotes the molar fraction of  $C_2H_{4-i}D_i$  in the gas phase and  $P_i$  and  $Q_i$  are the probabilities of the formation of  $C_2H_{4-i}D_i(a)$  from  $C_2H_{5-i}D_i(a)$  and  $C_2H_{4-i}D_{i+1}(a)$  by the reverse of step (III), respectively.

Eqn (17) gives five simultaneous equations for the respective i from 0 to 4 as shown by the following matrix:

$$\begin{bmatrix} b_0 & c_0 & 0 & 0 & 0 \\ a_1 & b_1 & c_1 & 0 & 0 \\ 0 & a_2 & b_2 & c_2 & 0 \\ 0 & 0 & a_3 & b_3 & c_3 \\ 0 & 0 & 0 & a_4 & b_4 \end{bmatrix} \begin{bmatrix} x_0 \\ x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} X_0 \\ X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix},$$
(18)

where  $a_i$ ,  $b_i$ ,  $c_i$  (i = 0, 1, 2, 3, 4) and the relative rate, R, are given by eqn (19)-(32):

$$b_{0} = 1 + \left[1 - \left(y_{\rm H} + \frac{f}{2 + f} y_{\rm D}\right)\right] R,$$
(19)

$$c_0 = -\frac{f}{2(2+f)} y_{\rm H} R, \tag{20}$$

$$a_1 = -\frac{2}{2+f} y_{\rm D} R, \tag{21}$$

$$b_{1} = 1 + \left\{ 1 - \left[ \left( \frac{1}{2} + \frac{1}{2+f} \right) y_{H} + \left( \frac{f}{1+2f} + \frac{f}{2(2+f)} \right) y_{D} \right] \right\} R,$$
(22)

$$c_1 = -\left(\frac{f}{2(1+2f)} + \frac{f}{2(2+f)}\right) y_{\rm H} R,$$
(23)

$$a_2 = -\left(\frac{1}{2+f} + \frac{1}{1+2f}\right) y_{\rm D} R,\tag{24}$$

$$b_{2} = 1 + \left[1 - \left(\frac{1}{2+f} + \frac{1}{4(1+2f)} + \frac{1}{4}\right)y_{H} - \left(\frac{f}{1+2f} + \frac{f}{4(2+f)} + \frac{1}{4}\right)y_{D}\right]R, \quad (25)$$

$$c_2 = -\left(\frac{f}{1+2f} + \frac{f}{2(2+f)}\right) y_{\rm H} R,\tag{26}$$

$$a_{3} = -\left(\frac{1}{2(1+2f)} + \frac{1}{2(2+f)}\right) y_{\rm D} R,\tag{27}$$

$$b_{3} = 1 + \left[1 - \left(\frac{1}{2(1+2f)} + \frac{1}{2+f}\right)y_{\mathrm{H}} - \left(\frac{1}{2} + \frac{f}{1+2f}\right)y_{\mathrm{D}}\right]R,$$
(28)

$$c_3 = -\frac{2f}{1+2f} y_{\rm H} R, \tag{29}$$

$$a_4 = -\frac{1}{2(1+2f)} y_{\rm D} R,\tag{30}$$

$$b_4 = 1 + \left(1 - \frac{1}{1 + 2f} y_{\rm H} - y_{\rm D}\right) R,\tag{31}$$

$$R = \overline{v}(\mathrm{III})/v_{\mathrm{s}}.\tag{32}$$

In the derivation of eqn (19)-(32) the following two assumptions were introduced. (1) The following two configurational isomers for  $C_2H_2D_2(a)$  form with an equal probability.

$$\underset{*}{\overset{CHD}{\leftarrow}--\underset{*}{\overset{CHD}{\leftarrow}}} \overset{CH_2}{\underset{*}{\overset{---CD_2}{\leftarrow}}}$$

(2) The isotopic effect in the rupture of carbon-hydrogen bonds is taken into account by a common factor f defined as the ratio of the ease of C—D rupture to that of C—H. Therefore, the probabilities of the rupture of C—H and C—D are exemplified as follows with respect to the methyl groups of  $-CH_2D$  and  $-CHD_2$ :

probability for   
C-H rupture 
$$\left( \frac{2}{2+f} \right)$$
 for  $-CH_2D$ ,  $\left( \frac{1}{1+2f} \right)$  for  $-CHD_2$ .  
probability for   
C-D rupture  $\left( \frac{f}{2+f} \right)$  for  $-CHD_2$ .

Here we have introduced the isotopic effect only for the rupture but not for the formation of carbon-hydrogen bonds because Guczi *et al.*<sup>11</sup> have concluded that the rate of catalytic hydrogen exchange between ethane and hydrogen is not influenced by the difference in the bond strengths between H—Ni and D—Ni.

In our calculations, values for the molar fraction of  $[{}^{2}H_{i}]$  ethylene in the gas phase,  $X_{i}$ , are equated as  $X_{0} = 1$ ,  $X_{1} = X_{2} = X_{3} = X_{4} = 0$  according to the experimental conditions. Eqn (18) is now solved for  $x_{i}$ , i = 0, 1, 2, 3, 4 by taking  $y_{D}$  and R as parameters. Then, using these values of  $x_{i}$ ,  $y_{i}$  is calculated from eqn (14) and the final D-atom distribution of ethane from eqn (15), respectively. We prepared two sets of D-atom distributions for the different values of R or  $y_{D}$  and they are summarised by eqn (16), where  $c_{1}$  and  $c_{2}$  are given by a parameter of r (0 < r < 1) as 1 - r and r.

#### Case 1. Two pathways for step (III).

Typical results calculated by assuming a pair of values for  $R[\dot{v}(III)/v_s]$  are exemplified in table 7. In calculations (1) and (2) two maxima are reproduced for the  $[{}^{2}H_{2}]$ - and  $[{}^{2}H_{6}]$ -ethanes although the isotopic effect was neglected (f = 1). One can see a sensitive effect of  $y_{D}$  on the distribution.

						$[^{2}H_{i}]$ ethane (%)							
calc.	$R_{1}/R_{2}$	r	f	$y_{\rm D}$	[ <sup>2</sup> H <sub>0</sub> ]	[ <sup>2</sup> H <sub>1</sub> ]	$[{}^{2}H_{2}]$	[ <sup>2</sup> H <sub>3</sub> ]	[ <sup>2</sup> H <sub>4</sub> ]	[ <sup>2</sup> H <sub>5</sub> ]	[ <sup>2</sup> H <sub>6</sub> ]	ethane	
(1)	0.4/50 0.4/50 0.4/50 0.4/50	0.5 0.5 0.5 0.5	1.0 1.0 1.0 1.0	0.90 0.91 0.92 0.94	0.42 0.34 0.27 0.15	7.67 6.95 6.22 4.73	36.03 36.50 36.98 37.95	9.91 9.88 9.89 9.96	8.23 7.66 7.11 6.08	16.83 16.32 15.68 14.00	20.90 22.33 23.84 27.13	0.59 0.59 0.60 0.61	
(2)	0.3/80 0.3/80 0.3/80 0.3/80	0.5 0.5 0.5 0.5	1.0 1.0 1.0 1.0	0.90 0.91 0.92 0.94	0.43 0.35 0.29 0.15	7.90 7.17 6.75 4.89	36.75 37.31 39.55 39.04	7.81 7.77 6.16 7.80	7.09 6.46 5.48 4.71	17.17 16.54 15.72 13.78	22.82 24.38 26.03 29.62	0.59 0.60 0.60 0.62	
(3) (4) (5) averag	0.04/10 0.04/10 0.04/0 ge in the T	0.6 0.4 0.6 afel reg	0.2 0.05 0.1 gion	0.90 0.90 0.87	0.45 0.45 0.76 0	8.23 8.13 10.35 6.2	38.17 37.60 36.01 38.9	7.83 6.98 7.44 6.7	8.66 7.34 8.32 8.0	14.06 12.97 14.41 13.8	22.60 26.52 22.70 24.4		

TABLE 7.—D-ATOM DISTRIBUTIONS IN ETHANE CALCULATED ON THE BASIS OF THE DUAL-PATHWAY MECHANISM (CASE 1)

A computer simulation was thus carried out to find values of the four parameters,  $R_1/R_2$ , r, f and  $y_D$ , for which the calculated D-atom distribution reproduces that observed within experimental error, *i.e.*  $d_o = 0$ ,  $2.5 < d_1 < 12.2$ ,  $36.4 < d_2 < 43.3$ ,  $5.6 < d_3 < 7.8$ ,  $7.1 < d_4 < 9.3$ ,  $11.4 < d_5 < 15.0$  and  $22.3 < d_6 < 30.1$  (table 1). The ranges of each parameter allowed are

$$\begin{cases} y_{\rm D} = 0.85 \cdot 0.92 \\ R_1/R_2 = (0.01 \cdot 0.4)/(9 \cdot 30) \\ f = 0.05 \cdot 0.3 \\ r = 0.4 \cdot 0.5. \end{cases}$$

$$(33)$$

Some examples of the D-atom distributions are listed in table 7, calculations (3)-(5).

The value of  $y_D$  in eqn (33) is reasonable when compared with the deuterium fraction of the solution used (0.88 at the end of the experiments). The estimated ratio of  $R_1/R_2$  shows that in one of the two pathways the backward rate of step (III),  $\dot{v}$ (III), is 1-40% larger than  $v_s$ , and in the other one  $\dot{v}$ (III) is larger by an order of magnitude. The isotopic effect, f, is allowed a rather wide range of 0.05-0.3 in harmony with the value of 0.2-0.3 reported on Ni by Flanagan and Rabinovitch.<sup>12</sup>

The result simulated at  $y_D = 0.92$ ,  $R_1/R_2 = 0.01/10$ , f = 0.1 and r = 0.4 is compared with the observed data in fig. 2. The agreement is satisfactory.

Case 2. Two pathways for step (V).

Another simulation was conducted by assuming a pair of values for  $y_D$  (the deuterium fraction of the adsorbed hydrogen). Some of the results are presented in

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FIG. 2.—Calculated D-atom distributions in ethane: (——), calculated distribution with  $y_D = 0.92$ ,  $\tilde{v}(III)/v_s = 0.01$  and 10, r = 0.4, f = 0.1; O, experimental results.

TABLE 8.—D-ATOM DISTRIBUTIONS IN ETHANE CALCULATED ON THE BASIS OF THE DUAL-PATHWAY MECHANISM (CASE 2)

							[²H <sub>i</sub> ]e	thane	(%)			D- fraction in
calc.	R	r	f	$y_{\rm D,1} / y_{\rm D,2}$	[ <sup>2</sup> H <sub>0</sub> ]	$[{}^{2}H_{1}]$	$[{}^{2}H_{2}]$	[ <sup>2</sup> H <sub>3</sub> ]	[ <sup>2</sup> H <sub>4</sub> ]	$[{}^{2}H_{5}]$	$[{}^{2}H_{6}]$	ethane
(1)	30	0.6	0.3	0.2/0.9	9.40	17.75	19.36	12.91	7.59	11.09	21.90	0.521
(2)	30	0.5	0.3	0.2/0.9	7.84	14.92	16.84	11.63	7.87	13.56	27.35	0.578
(3)	25	0.6	0.3	0.2/0.95	10.30	18.11	19.11	12.37	6.70	8.27	25.14	0.521
(4)	30	0.4	1.0	0.3/0.95	6.63	13.62	15.06	10.19	8.65	15.99	29.85	0.613
(5)	50	0.5	1.0	0.3/0.9	7.42	16.44	17.24	11.21	9.65	17.13	20.93	0.557
average	in the	Tafel	regior	ı (	)	6.2	38.9	6.7	8.0	13.8	26.4	

table 8. The calculated distributions also show two maxima for the  $[{}^{2}H_{2}]$ - and  $[{}^{2}H_{6}]$ -ethanes but their quantitative agreement is poor, especially for  $[{}^{2}H_{0}]$  to  $[{}^{2}H_{3}]$ . We varied the values of four parameters over a wide range but could not improve the distribution. Therefore we exclude the possibility of case 2.

## APPLICABILITY OF THE DUAL-PATHWAY MECHANISM TO OTHER RESULTS

The previous results obtained from  $C_2H_4 + D_2$  in HClO<sub>4</sub> solution for open-circuit (fig. 3, open circles)<sup>3</sup> are satisfactorily reproduced by the present dual-pathway model (solid curve) with values for *R*, *r* and *f* similar to those in fig. 2 but not for  $y_D$ ;  $R_1/R_2 = 0.01/10$ , r = 0.4, f = 0.1. The factor  $y_D$  has to be lowered to 0.15. Such a low value is attributed to the replacement of D(a) by H(a) from the HClO<sub>4</sub> solution *via* step (V).

Langer *et al.*<sup>6</sup> measured the D-atom distribution of ethane formed by the electrogenative hydrogenation of  $C_2H_4$  in DClO<sub>4</sub> solution. Their results (fig. 4, open circles) are satisfactorily reproduced by the present mechanism with the values of  $R_1/R_2 = 1/40$ , r = 0.3,  $f_D = 0.3$  and  $y_D = 0.25$ . The low value of  $y_D$  suggests that the deuterated water near the surface was diluted to a considerable extent by the continuous operation of the cell under a constant feed of light ethylene.

Results of Bond,<sup>13</sup> which are identical to those of Sato *et al.*,<sup>14</sup> are quoted in fig. 5. These results are obtained by the deuteration of light ethylene on platinized Pt



FIG. 3.—Calculated D-atom distribution for the previous results obtained from  $C_2H_4 + D_2$  in HClO<sub>4</sub> on open-circuit. Parameters are  $y_D = 0.15$ ,  $\overline{v}(III)/v_s = 0.01$  and 10, r = 0.4 and f = 0.1;  $\bigcirc$ , experimental results.<sup>3</sup>



FIG. 4.—Calculated D-atom distribution for the results of Langer *et al.*<sup>6</sup> Parameters are  $y_D = 0.25$ ,  $\dot{v}(III)/v_s = 1$  and 40, r = 0.4 and f = 0.3;  $\bigcirc$ , experimental results (46 mA, 0.143 V, 9.2% conversion).<sup>6</sup>



FIG. 5.—Calculated D-atom distributions for the results of Bond.<sup>13</sup> Experimental results:  $\bigcirc$ , platinized Pt, 297.5 K, 44% conversion;  $\triangle$ , Pt-Al<sub>2</sub>O<sub>3</sub>, 273 K, 51% conversion. Parameters are  $y_D = 0.3$ ,  $\dot{v}(III)/v_s = 0.1$  and 20 (for  $\bigcirc$ ) and 0.1 and 9 (for  $\triangle$ ), r = 0.4 (for  $\bigcirc$ ) and 0.5 (for  $\triangle$ ) and f = 0.3.

(circles) and Pt-Al<sub>2</sub>O<sub>3</sub> (triangles) in gas phase. Lines in the figure show the distributions calculated by the present method with the values of parameters R, r and f of eqn (33) and a value of  $y_D$  which is here 0.3. The lower value of 0.3 is due to dilution by light hydrogen from the reactant; in this case step (V) of scheme (1) is absent. The agreement in fig. 5 is satisfactory.

Thus the dual-pathway mechanism is also concluded to operate in gas-phase heterogeneous reduction.

# REACTIVITY OF THE ADSORBED HYDROGEN ATOMS IN DIFFERENT ADSORPTION STATES

There are several adsorption states of hydrogen on a platinum electrode. Two of them are predominant as shown by a voltammogram (fig. 6, curve 1). According to Hubbard *et al.*<sup>15</sup> and Ross,<sup>16</sup> the left-hand peak (weakly adsorbed) is ascribed to H(a) on the (111) crystal plane and the right-hand peak (strongly adsorbed) to that on the (100) plane, respectively. In what follows we discuss their reactivities.

FIG. 6.—Voltammogram in the hydrogen region (curve 1, sweep rate; 0.3 V s<sup>-1</sup>, 1 mol dm<sup>-3</sup> HClO<sub>4</sub>). Curve 2, eqn (36); curve 3, eqn (34); curve 4, eqn (35).

Curve 1 in fig. 6 is reproduced by curve 2 which is the sum of two peaks (curves 3 and 4), expressed by the formulae of the Gaussian distribution, eqn (34) and (35). The current for charging the double layer,  $i_d$ , was taken as 0.25 mA over the whole potential range.

$$i_1/mA = 3.45 \times \exp[-1.45 \times 10^{-4} (\phi/mV - 80)^2],$$
 (34)

$$i_2/mA = 2.0 \times \exp[-1.45 \times 10^{-4} (\phi/mV - 240)^2],$$
 (35)

$$i = i_1 + i_2 + i_d.$$
 (36)

In the above equations, 3.45 and 2.0 are peak currents, 80 and 240 are peak potentials and  $1.45 \times 10^{-4}$  is an adjustable parameter. It is important to note that the weakly



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adsorbed hydrogen atom peak starts to increase with the shift of potential from ca. 0.25 V to less positive values in correspondence with the behaviour of the reduction current of ethylene. This implies that the weakly adsorbed hydrogen atom is important in the reduction.



FIG. 7.—Time variation of current at 0.13 V. Curve 1, reduction without ageing after activation of the electrode; curves 2 and 3, reductions after ageing at 0.13 and 0.20 V, respectively, for 25 min.

In addition, the ethylene reduction current at  $\phi = 0.13$  V decreases with time during the reaction as shown by the broken line in fig. 7. This deactivation is thought to be due to the conversion of the hydrogen atom from weak to strong adsorption.<sup>1, 3</sup> Thus, the activation of the electrode was followed by ageing in the same blank solution for 25 min at 0.13 V, when the weakly adsorbed hydrogen was expected to decrease. Then the reduction of ethylene was initiated at the same potential (line 2). The reduction current almost follows the time variation expected from line 1. Furthermore, line 3 was obtained by reduction at the same potential of 0.13 V, following the ageing at 0.2 V for 25 min. The reduction current almost follows line 1 from the beginning. The absence of the ageing effect is attributed to the absence of the weakly adsorbed



FIG. 8.—Effect of Cl<sup>-</sup> on the reduction of ethylene (curve 1) and the hydrogen evolution (curve 2). Curve 1 was obtained at  $p(C_2H_4) = 11$  cmHg without Cl<sup>-</sup>.  $\bigcirc$ ,  $\triangle$  and  $\square$  were obtained at Cl<sup>-</sup> concentrations of 10<sup>-4</sup>, 10<sup>-3</sup> and 10<sup>-2</sup> mol dm<sup>-3</sup>. Curve 2 was obtained under the same conditions without  $C_2H_4$ .

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hydrogen at 0.2 V, as seen from fig. 6. The polarization to 0.13 V after the ageing reviews the supply of weakly adsorbed hydrogen atoms.

Fig. 8 shows the Tafel plots for the reduction of ethylene (solid curve 1) and for the hydrogen evolution reaction (solid curve 2) in perchloric acid solution. The symbols,  $\bigcirc$ ,  $\triangle$  and  $\square$  represent the results obtained by successive additions of HCl at various concentrations. Under these conditions the plots are not influenced by the presence of chloride ion. Huang et  $al_{.,17}$  however, report the effect of Cl<sup>-</sup> on the adsorption state of hydrogen, *i.e.* the strongly adsorbed hydrogen is diminished with an increase of Cl<sup>-</sup> concentration but the weakly adsorbed is hardly affected.

From the above we conclude that only the weakly adsorbed hydrogen atom is active for the reduction of ethylene. The same conclusion has been derived in the reduction of buta-1,3-diene on a platinum electrode from voltammograms obtained during the reaction.<sup>18</sup> Therefore, the dual-pathway mechanism cannot be ascribed to the two differently adsorbed hydrogen atoms. This deduction is in agreement with the fact that the D-atom distribution of ethane is independent of potential over the Tafel relation region (table 1), in spite of the marked change in the relative amounts of the two types of adsorbed hydrogen atoms with potential (fig. 6).

# ORIGIN OF THE DUAL-PATHWAY MECHANISM

One possible cause of the dual-pathway mechanism would be the existence of different adsorption states of ethylene. An infrared study reveals two types of adsorbed ethylene, *i.e.*  $\pi$  and  $\sigma$  types on a platinum catalyst.<sup>19</sup> The signal of the  $\pi$ -type ethylene diminishes rapidly on the introduction of hydrogen, and gas-phase ethane is formed.<sup>19</sup> On the other hand, the  $\sigma$ -type ethylene, reported earlier,<sup>20</sup> corresponds to the rapid H/D exchange during the hydrogenation.<sup>7</sup> Ethylenes adsorbed in different manners are the cause for the dual-pathway mechanism.

# COINCIDENCE OF THE RESULTS FROM OPEN-CIRCUIT AND **ELECTROREDUCTIONS**

The coincidence between the D-atom distributions of runs 1 and 2 in table 4 shows that the same mechanism for the surface process is operative in the open-circuit and electroreductions. The difference in the mode of hydrogen supply does not have any effect on the present reaction. We have concluded that the hydrogen molecule takes part in the reduction of buta-1,3-diene through the weakly adsorbed hydrogen atom.<sup>18</sup> This will be also the case in the reduction of ethylene.

Another coincidence has been found between the Tafel line of the electroreduction and the plot of the logarithm of the reduction rate (as current) against the open-circuit potential.<sup>4</sup> The coincidence suggests that step (V) of scheme (1) is in equilibrium in both cases of reduction.

# CONCLUSIONS

(1) The reduction of ethylene on a platinum electrode in acid solution proceeds through two pathways. (2) These two pathways differ in the reversibility of the elementary step

$$C_2H_4(a) + H(a) \rightleftharpoons C_2H_5(a)$$

which causes the H/D exchange between the reaction intermediates and the electrolyte solution. (3) The difference in reversibility cannot be attributed to a difference in the adsorption states of hydrogen. Only the weakly adsorbed hydrogen atom is reactive. (4) One possible cause would be the difference in the adsorption states of ethylene. (5) The difference in the mode of hydrogen supply, *i.e.*  $H^++e^-$  or  $H_2$ , does not have

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any effect on the reaction rate, the D-atom distributions, and hence on the reaction mechanism.

We thank Prof. Hisao Kano, Muroran Institute of Technology, for constant encouragement given throughout the present work. This paper is partly taken from the *Ph.D. Thesis* of Keikichi Fujikawa presented to Hokkaido University.

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