

# Hydrogenation of Ethylene on Metal Electrodes

## Part 2.—Structure of the Adsorption Layer on Platinum at a Working Condition on Open Circuit

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The structure of the adsorption layer was studied by the potential sweep method on a platinum electrode in 1 N HClO<sub>4</sub> solution saturated with a reaction gas of various compositions (mixtures of H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and He). Results show that the structure of the adsorption layer satisfies previous predictions on the rate-determining step and that the open circuit potential is determined by the equilibrium condition of the step,  $H^+ + e^- \rightleftharpoons H(ads)$ . The large change in the hydrogen peak caused by standing the electrode in the solution is in agreement with the decay of the catalytic activity for the hydrogenation of ethylene.

There is much published work on the adsorption of ethylene on Pt electrode.<sup>1</sup> However, the systems studied contain only ethylene as an adsorbate with an inert gas such as nitrogen or a rare gas as diluent. The presence of hydrogen gives rise to competitive adsorption onto the surface and produces hydrogenation of ethylene. The kinetics of the hydrogenation in such conditions has been studied in our previous paper.<sup>2</sup> The purpose of the present paper is to study the relationship between the structure of the adsorbed layer on the Pt electrode surface and the kinetics of hydrogenation.

We concluded previously<sup>2</sup> that the reduction of ethylene with hydrogen at the Pt electrode on open circuit is controlled by the rate of diffusion of H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>, depending on whether  $P_H/P_E < 5.6$  or  $> 5.6$ , respectively, where  $P_H$  and  $P_E$  represent partial pressures of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. The open circuit potential, which reflects the state of the surface, was found to be close to the reversible value of the hydrogen electrode at  $P_H/P_E > 5.6$ , but to deviate greatly in the anodic direction at  $P_H/P_E < 5.6$ .

Consequently, the electrode surface is expected to have an adsorbed layer of a different structure depending on the value of the ratio,  $P_H/P_E$ .

## EXPERIMENTAL

The apparatus, material and cell have been described.<sup>2</sup>

### ELECTRODE

Smooth platinum wire (diam., 0.5 mm; length, 10 cm) in the main compartment of the cell was used as a test electrode and was located at the centre of a platinized cylindrical Pt net (apparent area, 43.5 cm<sup>2</sup>) which served as a counter electrode. The reference electrode was a platinized Pt wire and was separated from the main compartment by a fritted glass disc and a closed Teflon tap. Purified hydrogen at 1 atm was always bubbled through the reference electrode compartment.

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## ELECTRICAL CIRCUIT

A generator, GEN 1 (series 160, Tektronix), gives two signals, one of which triggers an oscilloscope (type 5302 with differential preamplifier, SP-02DFH-A, Iwasaki Communication Apparatus Ltd., Japan) and the other operates the other generator, GEN 2 (Function Generator 3300A with plug-in unit, 3302A, Hewlett Packard), with a time delay of about 20 ms. A triangular pulse of potential was applied from GEN 2 to the interface of the test electrode through a potentiostat (V8, Yanagimoto Mfg. Co. Ltd., Japan). The potential output of the potentiostat was initially adjusted to the open circuit potential of Pt by a battery through the d.c. offset of GEN 2. The potential of the test electrode was thus swept in the anodic direction up to 1.8 V against the open circuit potential and then reversed. Current was observed, as a potential drop across a calibrated resistor of 1 ohm, on the oscilloscope. Sweep rate of potential in a triangular pulse was  $14.4 \text{ V s}^{-1}$  in most cases.

## PROCEDURE

The cell was first cleaned with acetone and then with 1 N  $HNO_3$  solution. After platinization of the counter and reference electrodes, the cell was thoroughly rinsed with triply distilled water. An electrolyte solution was then introduced and deaerated by bubbling purified hydrogen through it, at least overnight. The test electrode was activated by anodic polarization at 1.8 V (r.h.e.) for 2 min and kept in the solution on open circuit for 2 min as described previously.<sup>2</sup> Then a reaction gas which was prepared in the circulation system ( $557 \text{ cm}^3$ ) from the purified  $C_2H_4$ ,  $H_2$  and He (total pressure, 76 cmHg), was circulated through the cell. The final composition of the gas was estimated by correcting for the hydrogen present in the gas phase of the main compartment ( $151 \text{ cm}^3$ ). The flow rate was kept constant throughout the work ( $10 \text{ dm}^3 \text{ min}^{-1}$ ). Fig. 1<sup>2</sup> shows typical time-variations of the open circuit potential after the introduction of reaction gas. The potential shifts rapidly in the anodic direction and then stays constant or decreases gradually after passing through maximum, depending on the gas composition. Five minutes later when the rate of potential change becomes small, the electrode was treated by the successive application of four or five triangular pulses at intervals of 1 s. These pulses (potential width, 1.8 V in the anodic direction; sweep rate  $14.4 \text{ V s}^{-1}$ ) were superposed on the open circuit potential at 5 min.

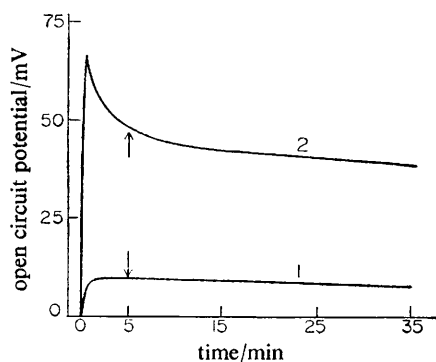


FIG. 1.—Open circuit potential of the Pt electrode after the introduction of the reaction gas in 1 N  $HClO_4$ .<sup>2</sup>  $P_H$  and  $P_E/\text{cmHg}$  are: 1, 31.9 and 2.0; 2, 31.9 and 19.6. Arrows indicate the potential at which several pulses were successively applied to obtain a reproducible surface state.

The  $i$  against  $V$  curve was reproducible after the 2nd or 3rd pulse. This treatment was carried out to obtain a reproducible surface state at a given condition and will be called "pre-conditioning". A single triangular pulse with the same potential width and sweep rate was then applied as a function of the time after the pre-conditioning (standing time), i.e., at 1, 2, 5, 10, 30, 60, 120 or 300 s, during which time the electrode was kept at the open

circuit potential obtained at 5 min. Whenever the gas was replaced with other mixtures (table 1), the main compartment was first saturated with  $H_2$  and then the same procedure was repeated. All measurements were carried out at room temperature (25-28°C). Potentials in the text are referred to the reversible hydrogen electrode (r.h.e.) in the same solution and at 1 atm  $H_2$ .

TABLE 1.—COMPOSITION OF REACTION GASES STUDIED

run	$P_H/\text{cmHg}$	$P_E/\text{cmHg}$	$P_H/P_E$	region
DE-1	72.8	3.2	24.0	E
DE-2	53.6	3.2	16.7	E
DE-3	47.7	3.1	15.4	E
DE-4	41.8	3.1	13.5	E
DE-5	38.7	3.9	9.8	E
DH-1	7.9	4.0	2.0	H
DH-2	7.9	5.5	1.4	H
DH-3	7.9	5.6	1.4	H
DH-4	15.1	7.9	1.92	H
DH-5	15.1	15.8	0.96	H
DH-6	15.1	23.6	0.64	H
DH-7	15.1	23.6	0.64	H
DH-8	15.1	35.4	0.43	H
DH-9	23.0	15.8	1.46	H
DH-10	30.9	15.8	1.96	H
DH-11	38.7	15.8	2.45	H
E-1	0	15.8	—	—
E-2	0	7.9	—	—
E-3	0	3.9	—	—
H-1	15.1	0	—	—
H-2	30.9	0	—	—
H-3	38.7	0	—	—
H-4	76	0	—	—

## RESULTS

 $i$  AGAINST  $V$  CURVE WITH  $H_2$ 

We first represent the results obtained in the solution saturated only with  $H_2$ . Fig. 2 shows typical  $i$  against  $V$  curves observed at different standing times (for run, H-3 in table 1). For the oxidation wave, the intensity of the peak at *ca.* 0.16 V (peak I) decreases with standing time ( $\tau$ ), whereas the peak at *ca.* 0.30 V (peak II) first increases slightly and then decreases. The hump at 0.4-0.6 V grows with  $\tau$ . The peak at 1.0 V remains almost constant but the current at potentials more positive than *ca.* 1.2 V increases with  $\tau$ . After 300 s, the time-variation of the  $i$  against  $V$  curve becomes very small. Successive application of a few pulses always gives the initial  $i$  against  $V$  curve observed at  $\tau = 1$  s (curve 1).

The returning half of the  $i$  against  $V$  curve gives almost constant peaks for the reduction of surface oxygen and for the formation of adsorbed hydrogen atoms irrespective of  $\tau$ .

The minimum current in the oxidation wave increases slightly with  $\tau$ . When the current at 0.7 V,  $i_d$ , is plotted against the square root of the standing time,  $\sqrt{\tau}$ , one obtains a linear relation. Extrapolation of this relation to  $\tau = 0$  gives the values,

HYDROGENATION OF  $C_2H_4$  ON Pt ELECTRODES

3.5, 4.1 and 6.0  $\text{mA cm}^{-2}$  at  $P_H = 15.1$ , 30.9 and 76 cmHg, respectively. These values at  $\tau = 0$  are expressed by the equation,

$$i_d(\tau = 0)/(\text{mA cm}^{-2}) = 2.8 + 0.046(P_H/\text{cmHg}).$$

The second term on the right hand side of this equation at  $P_H = 76$  cmHg gives 3.5  $\text{mA cm}^{-2}$ , which is equal to the observed limiting current, 3.8  $\text{mA cm}^{-2}$ , for the

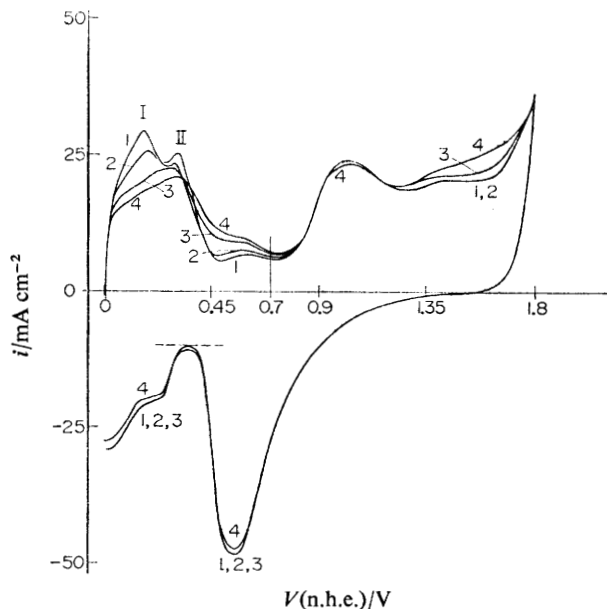


FIG. 2.—The  $i$  against  $V$  curve on Pt as a function of the standing time. Standing time/s: 1, 1; 2, 10; 3, 60; 4, 120. Solution is 1 N  $HClO_4$  saturated with  $H_2$  at 38.7 cmHg (H-3 in table 1). Sweep rate =  $14.4 \text{ V s}^{-1}$ .

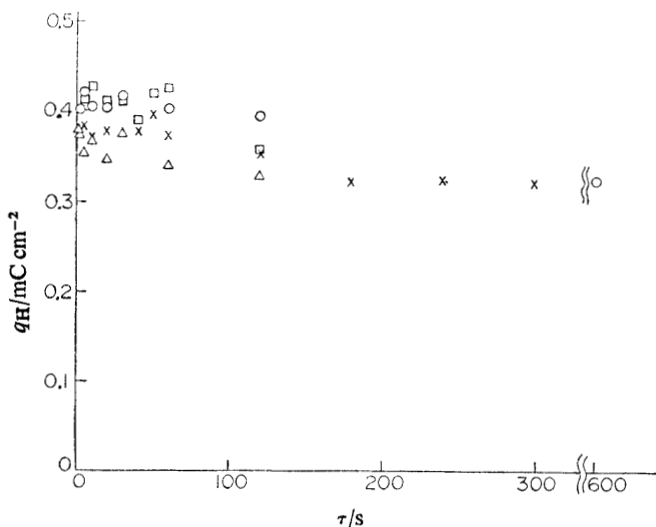


FIG. 3.— $q_H$  of Pt electrode in 1 N  $HClO_4$  as a function of the standing time.  $P_H/\text{cmHg}$ :  $\times$ , 15.1 (H-1 in table 1);  $\square$ , 30.9 (H-2);  $\Delta$ , 38.7 (H-3);  $\circ$ , 76 (H-4).

ionization of  $\text{H}_2$  dissolved in the solution at 1 atm.<sup>2</sup> The constant term,  $2.8 \text{ mA cm}^{-2}$ , represents a charging current of the double layer. A value of  $2.8 \text{ mA cm}^{-2}$  gives a capacity of  $190 \mu\text{F cm}^{-2}$  which is in good agreement with a literature value<sup>3</sup> of  $175 \mu\text{F cm}^{-2}$  obtained from the  $i$  against  $V$  curve under bubbling of  $\text{N}_2$ .

The charge required to oxidize the adsorbed hydrogen,  $q_{\text{H}}$  ( $\text{mC cm}^{-2}$ ), was estimated by integrating the current above  $i_d(\tau = 0)$  over the potential range up to 0.7 V. Fig. 3 shows  $q_{\text{H}}$  as a function of  $\tau$  (for runs, H-1 to -4 in table 1).  $q_{\text{H}}$  is almost constant, though with a slight decrease. Its final value is  $0.32 \text{ mC cm}^{-2}$ , independent of  $P_{\text{H}}$  at  $P_{\text{H}} > 15 \text{ cmHg}$ . This value will be denoted as  $s q_{\text{H}}$  in the following.

The effect of the sweep rate on  $q_{\text{H}}$  is to monotonously decrease  $q_{\text{H}}$  when the sweep rate exceeds *ca.*  $15 \text{ V s}^{-1}$ . Some adsorbed hydrogen atoms may remain unoxidized at rapid scanning of potential. A similar effect of sweep rate has been reported for  $\text{C}_2\text{H}_4$ .<sup>4</sup> Thus, a sweep rate of  $14.4 \text{ V s}^{-1}$  (4 Hz) was used in the present study.

The peak area for the reduction of surface oxygen was estimated by subtracting the residue current shown by the dotted line in fig. 2. The average value is  $0.55 \text{ mC cm}^{-2}$  at  $\tau = 300 \text{ s}$ . This value is 1.8 times larger than  $s q_{\text{H}}$ , which is close to 2, and suggests that the surface oxygen exists as adsorbed oxygen atoms occupying the same sites as hydrogen atoms.

#### $i$ AGAINST $V$ CURVE WITH $\text{C}_2\text{H}_4$

The  $i$  against  $V$  curve in the presence of  $\text{C}_2\text{H}_4$  is of the usual shape<sup>4</sup> as exemplified by curve 1 in fig. 4, where the curve in  $\text{H}_2$ , curve 2, is shown for comparison. In an ethylene atmosphere, the final value of the open circuit potential was found to be in the double layer region (e.g., 0.41 V in E-3).

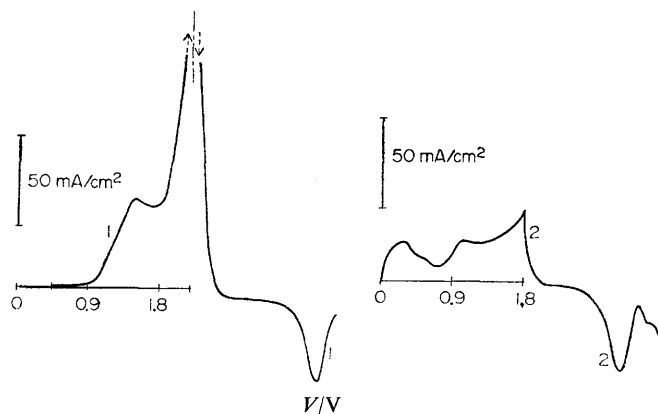


FIG. 4.—The  $i$  against  $V$  curves on Pt in 1 N  $\text{HClO}_4$  saturated with; 1,  $\text{C}_2\text{H}_4$  3.9 cmHg (E-3 in table 1); 2,  $\text{H}_2$  38.7 cmHg (H-3).  $\tau = 300 \text{ s}$ ; sweep rate =  $14.4 \text{ V s}^{-1}$ .

From the figure, one can see that on curve 1 (i) adsorbed hydrogen atoms are not observed and the current at 0.7 V reduces to almost zero, and (ii) the peak for the reduction of adsorbed oxygen atoms remains almost the same as that in  $\text{H}_2$ . The latter fact indicates that the surface polarized up to an inversion potential (1.8 V relative to the open circuit potential) is free from adsorbed ethylene species.

The net increase of the current in the potential range more positive than 0.7 V in the presence of  $\text{C}_2\text{H}_4$ ,  $\Delta q_0$ , was taken as the charge consumed in oxidizing the adsorbed ethylene species. To estimate  $\Delta q_0$ , curves 1 and 2 in fig. 4, both of which

are observed at the same  $\tau$ , are located by adjusting  $i_d$  values (i.e., the current at 0.7 V) to the same level and curve 2 was extrapolated according to the oxygen evolution current at higher potentials. The above estimation of  $\Delta q_0$  assumes constant  $i_d$  at potentials more positive than 0.7 V. The value of  $\Delta q_0$  was observed to be constant after 1 s which indicates fast adsorption of  $C_2H_4$ .

The effect of  $P_E$  on  $\Delta q_0$  is shown in fig. 5 where the last point marked with an asterisk, was obtained at  $\tau = 300$  s with added  $H_2$  at  $P_H = 15.1$  cmHg (DH-8). As will be seen later (fig. 7),  $q_H$  at  $\tau = 300$  s is negligible. Hence, the above value marked with an asterisk will be taken as  $\Delta q_0$  in the absence of  $H_2$ . The curve is a Langmuir isotherm, showing a saturation value,  $\Delta_s q_0$  of  $1.53 \text{ mC cm}^{-2}$ . This saturation value is 4.8 times larger than  $s q_H$ .

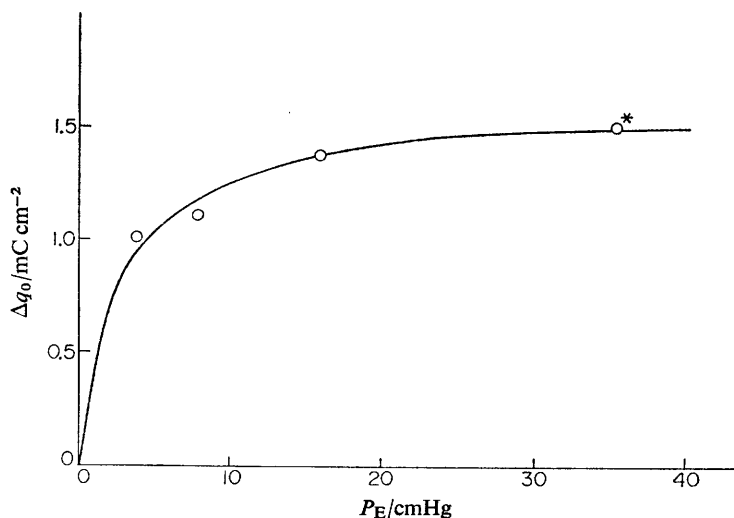


FIG. 5.—Adsorption isotherm of  $C_2H_4$  on Pt electrode in 1 N  $HClO_4$ . The curve is a Langmuir type.

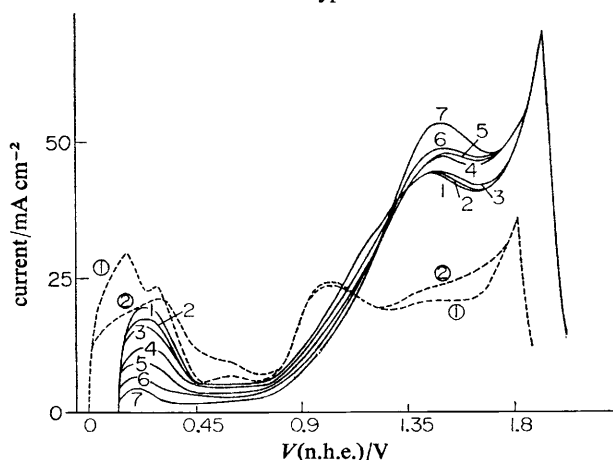


FIG. 6.—The  $i$  against  $V$  curve on Pt as a function of the standing time in 1 N  $HClO_4$  saturated with a reaction gas at  $P_H = 15.1$  and  $P_E = 15.8$  cmHg (DH-5 in table 1, region H). Dotted curves are obtained in the solution saturated with  $H_2$  at atmospheric pressure. Standing time/s: 1, 1; 2, 2; 3, 5; 4, 20; 5, 60; 6, 120; 7, 300;  $\odot$ , 1;  $\otimes$ , 300.

$q_H$  AND  $\Delta q_0$  AT A WORKING CONDITION ON OPEN CIRCUITS

When a mixture of  $H_2$  and  $C_2H_4$  is introduced, the hydrogenation of  $C_2H_4$  takes place on the electrode on open circuit. As described in the previous paper,<sup>2</sup> the reaction kinetics as well as the open circuit potential differ, depending whether the ratio of  $P_H/P_E$  is above or below 5-6. Different regions defined by the ratio are called regions E and H as indicated in table 1.

(1) REGION H.—At  $P_H/P_E < 5-6$ ,  $H_2$  diffusion is rate-controlling. The  $i$  against  $V$  curve in this region (DH-1 to 11) shows a single peak of rounded shape which decreases in size with  $\tau$  as shown in fig. 6 (DH-5). Such a decay does not produce the hump at 0.4-0.6 V as observed in  $H_2$  alone. However,  $i_d$  decays significantly with  $\tau$ , though a slight increase of  $i_d$  at the initial stage is apparent at high  $P_H$  (see fig. 8). Time-variations of  $q_H$ ,  $i_d$ , and  $\Delta q_0$  are shown in fig. 7 (DH-8).  $q_H$  and  $i_d$  decrease linearly with the logarithm of  $\tau$ .  $\Delta q_0$  is initially large and increases with  $\tau$ . Similar curves are obtained in all runs in region H.

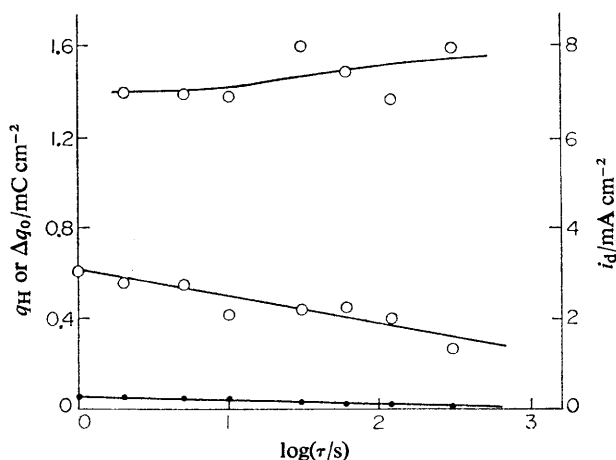


FIG. 7.—Time-variations of  $\Delta q_0$  (upper curve),  $i_d$  (middle curve) and  $q_H$  (lower curve) on Pt in 1 N  $HClO_4$  saturated with a reaction gas of  $P_H = 15.1$  and  $P_E = 35.4$  cmHg (DH-8 in table 1).

Time-dependence of  $q_H$  in region H is summarized in eqn (I)-(VI).

$$q_H = -106 \log(\tau/s) + 322 \text{ mC cm}^{-2} \quad \text{at } P_H = 38.7, P_E = 15.8 \text{ cmHg} \quad (\text{I})$$

$$q_H = -86 \log(\tau/s) + 257 \text{ mC cm}^{-2} \quad \text{at } P_H = 30.9, P_E = 15.8 \text{ cmHg} \quad (\text{II})$$

$$q_H = -69 \log(\tau/s) + 200 \text{ mC cm}^{-2} \quad \text{at } P_H = 23.0, P_E = 15.8 \text{ cmHg} \quad (\text{III})$$

$$q_H = -61 \log(\tau/s) + 171 \text{ mC cm}^{-2} \quad \text{at } P_H = 15.1, P_E = 15.8 \text{ cmHg} \quad (\text{IV})$$

$$q_H = -40 \log(\tau/s) + 119 \text{ mC cm}^{-2} \quad \text{at } P_H = 15.1, P_E = 23.6 \text{ cmHg} \quad (\text{V})$$

$$q_H = -20 \log(\tau/s) + 61 \text{ mC cm}^{-2} \quad \text{at } P_H = 15.1, P_E = 35.4 \text{ cmHg} \quad (\text{VI})$$

The above equations are summarized as

$$q_H = -(1/3.0) q_H(\tau = 1) \{ \log(\tau/s) - 3.0 \}, \quad (1)$$

where  $q_H(\tau = 1)$  is  $q_H$  at  $\tau = 1$  s.

The time-dependence of  $i_d$  in region H is summarized in fig. 8, where curves 1 to 4 are obtained at a constant  $P_E$  of 15.8 cmHg and 4 to 6 at a constant  $P_H$  of 15.1 cmHg.

Fig. 8 shows that  $i_d$  first increases slightly for a time which is longer for larger  $P_H$  and then, following the maximum, it decreases linearly with the logarithm of  $\tau$ . This linear relation may be expressed as

$$i_d = -(1/3.6) \times i_d(\tau = 1) \{\log(\tau/s) - 3.6\}, \quad (2)$$

where  $i_d(\tau = 1)$  is  $i_d$  at  $\tau = 1$  s. The time-dependences of  $i_d$  and  $q_H$  are of the same form.

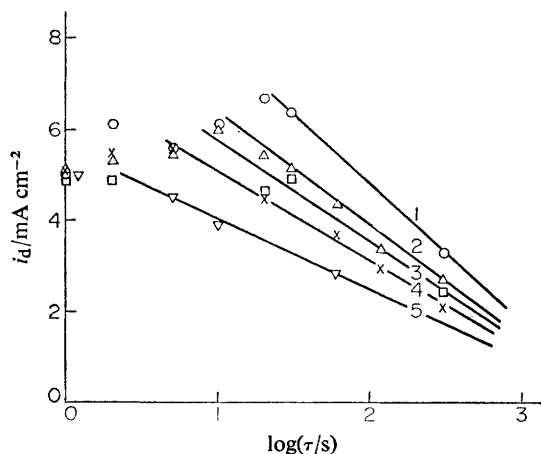


FIG. 8.—Time-variation of  $i_d$  on Pt in 1 N  $HClO_4$  saturated with a reaction gas of different compositions in region H.  $P_H$  and  $P_E/cmHg$ : 1, 38.7 and 15.8 (DH-11 in table 1); 2, 30.9 and 15.8 (DH-10); 3, 23.0 and 15.8 (DH-9); 4, 15.1 and 15.8 (DH-5); 5, 15.1 and 23.6 (DH-6); 6, 15.1 and 35.4 (DH-8).

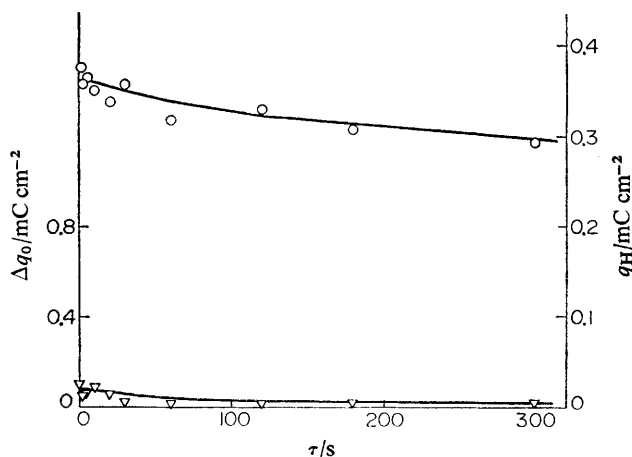


FIG. 9.—Time-variations of  $q_H$  (O) and  $\Delta q_0$  ( $\nabla$ ) on Pt electrode in 1 N  $HClO_4$  saturated with a reaction gas of  $P_H = 47.7$  and  $P_E = 3.1$  cmHg (DE-3 in table 1, region E).

With increase in the standing time, the electrode surface approaches a steady state at a given open circuit potential.  $\Delta q_0$  values at 300 s under a constant  $P_H$  of 15.1 cmHg are almost the same as those observed in  $C_2H_4$  alone (fig. 5).  $q_H$  values at 300 s become very small. Hence, it is concluded that the electrode surface



at the steady state is mainly covered with the ethylene species.  $q_H$  values for 300 s at a constant  $P_E$  are estimated from their dependences on  $\tau$ :

$$q_H \propto P_H^{1.1}. \quad (3)$$

$q_H$  values at constant  $P_H$  are so small that their dependence on  $P_E$  was not determined precisely.

(2) REGION E.—The  $i$  against  $V$  curve in this region is expected to reveal the presence of adsorbed hydrogen atoms characteristic of a given  $P_H$ , since the diffusion of  $C_2H_4$  is rate-controlling. Fig. 9 shows  $q_H$  and  $\Delta q_0$  as a function of  $\tau$  (DE-3).  $q_H$  is the same as in fig. 3 and its final value is equal to  $s q_H$  in all runs of region E (DE-1 to -5). Correspondingly,  $\Delta q_0$  is very small compared to the values in fig. 5 and decays with  $\tau$ .  $q_H$  and  $\Delta q_0$  at 300 s are shown in fig. 10 as a function of  $P_H$ .  $\Delta q_0$  values are small, far from its saturation value of  $1.53 \text{ mC cm}^{-2}$ . Thus, we conclude that in region E, the electrode surface is covered mainly with hydrogen atoms close to the saturation value and only a small amount of  $C_2H_4$  is adsorbed on the electrode surface.

$i_d$  in region E increases with  $\tau$  as in  $H_2$  alone.

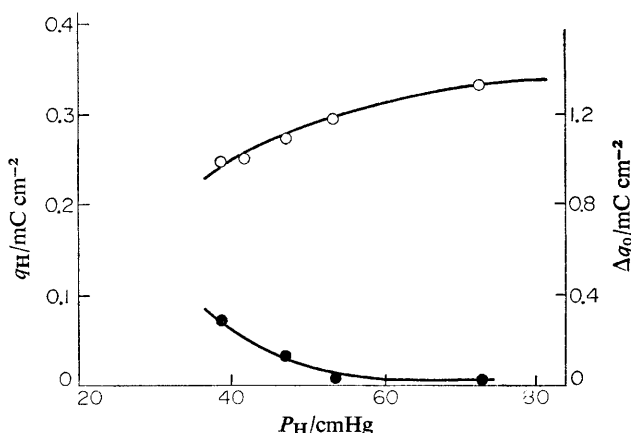


FIG. 10.—Dependence of  $q_H$  (○) and  $\Delta q_0$  (●) at  $\tau = 300$  s on  $P_H$  in region E.  $P_E = 3.1\text{--}3.9 \text{ cmHg}$ .

## DISCUSSION

### STATE OF THE ADSORBED HYDROGEN ATOM

Over a period of time the electrode in the solution saturated with 1 atm of  $H_2$  maintains a potential of zero volt (r.h.e.) and the amount of adsorbed hydrogen remains almost constant. The value of  $0.32 \text{ mC cm}^{-2}$  is close to  $0.296 \text{ mC cm}^{-2}$  reported by Gilman.<sup>4</sup> A value of  $0.21 \text{ mC cm}^{-2}$  has been quoted as the monolayer value for adsorbed hydrogen on Pt.<sup>5</sup> This value is obtained by assuming that the three principal lattice planes of (110), (100) and (111) occupy equal fractions on the surface. Each Pt atom is assumed to accommodate one hydrogen atom.<sup>6</sup> The observed value of  $0.32 \text{ mC cm}^{-2}$  is assumed to represent the value at full coverage, taking into account the roughness of the electrode surface.

Though the amount of adsorbed hydrogen remains almost constant, the shape of the hydrogen peaks reveals a large change. Peak I decreases with  $\tau$  but its decrease is largely compensated by the appearance of the hump at 0.4–0.6 V. Such compensation clearly indicates a change in the adsorbed state of hydrogen atoms to a more stable form.

Sasaki and Yoshida<sup>7</sup> studied the time-variation of the hydrogen peaks and found that the rate of decrease in the peak at *ca.* 0.15 V (peak I) is expressed by

$$\text{decrease} = k\sqrt{\tau} + k' \log \tau,$$

where *k* and *k'* are constants. The second term on the right hand side is predominant during the initial 10 min of  $\tau$ , which they attributed to the rearrangement of the surface hydrogen atoms. We note here our previous result that the amount of C<sub>2</sub>H<sub>6</sub> produced by the reduction of C<sub>2</sub>H<sub>4</sub> with H<sub>2</sub> on open circuit,<sup>2</sup> is expressed by a logarithmic function of the reaction time for the initial 10 min and subsequently by a square root function of time, indicating that the adsorbed hydrogen atoms responsible for peak I play an important role in the hydrogenation of C<sub>2</sub>H<sub>4</sub> on Pt.

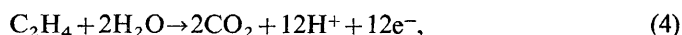
#### ADSORPTION OF ETHYLENE

$\Delta q_0$  consists of the amount of charge needed to oxidize the initially adsorbed ethylene species,  $q_E(\text{ads})$ , and C<sub>2</sub>H<sub>4</sub> which diffuses to the electrode,  $q_E(\text{diff})$ . Other contributions due to the changes of the double layer capacity and of the amount of adsorbed oxygen are reported to be small.<sup>4</sup>

$q_E(\text{diff})$  is estimated to a first approximation from the equation,<sup>4</sup>

$$q_E(\text{diff}) = 2nFcD^{\frac{1}{2}}\pi^{-\frac{1}{2}}t^{\frac{1}{2}},$$

where *n* is the number of electrons released by the oxidation of an adsorbed ethylene species, *c* the ethylene concentration in solution, *D* the diffusion constant, and *t* the pulse duration. Assuming *n* = 12 for



and  $D = 1.56 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for acetylene,<sup>7</sup> and using the relation<sup>2</sup>

$$c/\text{mol cm}^{-3} = (1.8 \times 10^{-3}/22\,400) \times P_E/\text{cmHg},$$

then

$$q_E(\text{diff}) = 0.41 \times P_E \times t^{\frac{1}{2}} \text{ mC cm}^{-2}. \quad (5)$$

Since the duration of the half pulse is 0.125 s,  $q_E(\text{diff})$  becomes  $0.146 \times P_E \text{ mC cm}^{-2}$ , which is comparable in magnitude with the observed  $\Delta q_0$ . Despite this, we concluded that there is no significant contribution of  $q_E(\text{diff})$  to  $\Delta q_0$  since, if there were, an increase in  $P_E$  would not lead to a limiting value of  $\Delta q_0$  (fig. 5). Thus, new sites formed by the oxidative desorption of the species will be covered preferentially by oxygen atoms. The oxygen covered surface is free from C<sub>2</sub>H<sub>4</sub> adsorption because in fig. 4 the peak for reduction of the adsorbed oxygen atom is unchanged in the presence of C<sub>2</sub>H<sub>4</sub>. Hence,  $\Delta q_0$  will represent the quantity of adsorbed species of ethylene.

Gileadi *et al.*<sup>9</sup> studied the adsorption isotherm of C<sub>2</sub>H<sub>4</sub> on a Pt-plated gold electrode in 1 N H<sub>2</sub>SO<sub>4</sub> solution and found that the coverage reaches a saturation value when the bulk concentration exceeds  $2 \times 10^{-8} \text{ mol cm}^{-3}$ . Their value, however, is extremely small compared to the value  $1.2 \times 10^{-6} \text{ mol cm}^{-3}$  expected from the present critical value of  $P_E$  (= 15 cmHg) required to attain 90 % of the saturation value (fig. 5) and the solubility constant in HClO<sub>4</sub> solution,  $1.8 \times 10^{-3} \text{ cm}^3 \text{ (s.t.p.) (cm}^3 \text{ soln.)}^{-1} \text{ cmHg}^{-2}$ . Gilman<sup>10</sup> reported a value of  $0.62 \pm 0.02 \text{ mol cm}^{-2}$  (geometrical) for  $\Delta q_0$  at 0.2–0.4 V and  $1.3 \times 10^{-4}$ –0.114 atm. His value is 2.5 times smaller than the present  $\Delta_s q_0$  of  $1.53 \text{ mC cm}^{-2}$  (geometrical). In the present study  $\Delta_s q_0$  was reached at  $P_E$  values  $\geq 15 \text{ cmHg}$  which exceed the pressure range studied by Gilman.

Gilman calculated the number of hydrogen sites obscured per molecule of adsorbed

acetylenic species to be 3. The present value of  $1.53 \text{ mC cm}^{-2}$  for  $\Delta_s q_0$  which is 4.8 times larger than  $s q_H$  gives 2.1 for the number of sites obscured by an acetylenic species. One of the reasons for our smaller value is the larger value of  $\Delta_s q_0$ . Another reason may be the overestimation of  $\Delta_s q_H$  in the work of Gilman. As seen from fig. 6 of ref. (4), the current against voltage curve in the hydrogen evolution region shifts in the negative direction in the presence of  $\text{C}_2\text{H}_4$  and thus extrapolation of the hydrogen peak will result in a larger value of  $\Delta_s q_H$ .

When molecular adsorption of  $\text{C}_2\text{H}_4$  is assumed, the number of sites obscured becomes 2.5 on the basis of eqn (4). In our work<sup>11</sup> on the isotopic exchange reaction between  $\text{D}_2$ ,  $\text{C}_2\text{D}_4$  and  $\text{H}_2\text{O}$ , molecular adsorption was confirmed under the present experimental conditions. Hence, in the following discussion we assume ethylene molecules to be the adsorbed species.

#### ADSORPTION OF BOTH HYDROGEN AND ETHYLENE

When a reaction gas is introduced, the open circuit potential shifts instantaneously in the anodic direction as illustrated in fig. 1. After 5 min, the electrode was subjected to the pre-conditioning.

(1) In region E, the time-variation of  $q_H$  after the pre-conditioning (fig. 9) reproduces fig. 3, showing that the electrode surface is essentially the same as that in  $\text{H}_2$ . The change in the adsorption state of hydrogen atoms is similarly observed.

$\Delta q_0$  in fig. 9, however, shows the existence of an initial small amount of adsorbed ethylene. This ethylene might be brought to the surface during a period of 1 s between the pre-conditioning and first pulse.  $\Delta q_0$  in fig. 9, is  $0.10 \text{ mC cm}^{-2}$  at  $\tau = 1 \text{ s}$  and  $P_E = 3.2 \text{ cmHg}$  (DE-2). The time required for the diffusion of this amount of  $\text{C}_2\text{H}_4$  is calculated from eqn (5) as 5.6 ms. It is, however, interesting to see that the potential range swept during 5.6 ms is 80 mV (sweep rate,  $14.4 \text{ V s}^{-1}$ ) and is in agreement with that observed for the double layer region in the returning half of the  $i$  against  $V$  curve shown in fig. 2; in the double layer region, the current reaches a minimum. Since  $\text{C}_2\text{H}_4$  adsorption was concluded not to occur on the oxygen covered surface, it will take place on the bare surface provided by the removal of the adsorbed oxygen atoms during the last cathodic pulse of the pre-conditioning. When the potential of the last cathodic pulse passes into the hydrogen peak region, adsorbed hydrogen atoms are formed potentiostatically, preventing further adsorption of  $\text{C}_2\text{H}_4$ .

The gradual decrease of  $\Delta q_0$  with  $\tau$  shown in fig. 9 is attributed to the consumption of  $\text{C}_2\text{H}_4$  by hydrogenation.

(2) In region H, the adsorbed hydrogen atoms are not in equilibrium with  $\text{H}_2$  in solution.

The above conclusion that adsorbed  $\text{C}_2\text{H}_4$  is formed during the charging up of the double layer in the last cathodic sweep of the pre-conditioning, applies also to all runs in region H. Fig. 11 shows initial  $\Delta q_0$  and  $q_H$  values, i.e., values at  $\tau = 2 \text{ s}$  as a function of  $P_H$ . In fig. 11, a decrease of  $\Delta q_0$  accompanies an increase of  $q_H$ , in the ratio of 4.8 : 1 as seen from the absolute magnitude of their slopes, which is the same as the ratio of  $\Delta_s q_0 / s q_H$ . This result indicates that all sites available for adsorption are covered with either hydrogen atoms or ethylene molecules.

Changes of  $i_d$  and  $q_H$  with  $\tau$  shown in fig. 8 and eqn (I)-(VI) is explained as follows. The initial increase of  $i_d$  at relatively high  $P_H$  is attributed to the stabilization of the adsorbed hydrogen atoms as seen from the growing hump in fig. 2, so that the number of atoms which are oxidizable at 0.7 V is increasing with  $\tau$ . However,  $i_d$  starts to decrease after a certain time which is shorter the smaller is  $P_H$ . The hydrogenation

process is consuming adsorbed hydrogen atoms and hydrogen atom supply by diffusion is rate-determining in this region. Hence, the number of adsorbed hydrogen atoms on the surface is becoming less as  $\tau$  increases. Rates of decrease of  $i_d$  and  $q_H$  obey the same functional form, given by eqn (1) and (2), indicating the presence of a blocking effect on the surface. Vacant sites provided by the consumption of the adsorbed hydrogen will be covered with  $C_2H_4$ . On the ethylene-covered surface, the dissociation of  $H_2$  will not take place.

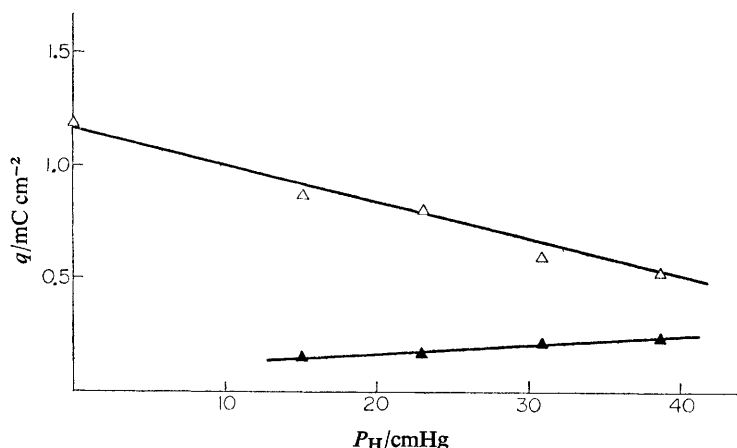


FIG. 11.—Dependence of  $q_H$  ( $\blacktriangle$ ) and  $\Delta q_0$  ( $\triangle$ ) at  $\tau = 2$  s on  $P_H$  in region H.  $P_E = 15.8$  cmHg.

The rate of consumption of adsorbed hydrogen is given by differentiation of eqn (1) as  $-dq_H/d\tau = q_H(\tau = 1)/(6.9 \times \tau)$ . The rate is proportional to the initial quantity of adsorbed hydrogen and inversely proportional to  $\tau$ , in agreement with the decay of the catalytic activity of the electrode for the hydrogenation of  $C_2H_4$ .<sup>2</sup>

The consumption rate is estimated from eqn (1) as  $2.9 \mu C s^{-1} cm^{-2}$  at  $\tau = 10$  s and  $P_H = 23.0$  cmHg (DH-9,  $P_E = 15.8$  cmHg), which corresponds to  $8.7 \times 10^{-10}$  mol min<sup>-1</sup> cm<sup>-2</sup>. This rate is extremely small compared with the observed rate of hydrogenation under the same conditions, i.e.,  $1.0 \times 10^{-7}$  mol min<sup>-1</sup> cm<sup>-2</sup> ( $k_H = 2.0 \times 10^{-7}$  mol min<sup>-1</sup> cmHg<sup>-1</sup> for 43.5 cm<sup>2</sup>).<sup>2</sup> Hence, the rate estimated from eqn (1) does not represent the rate of the surface hydrogenation of  $C_2H_4$ . The hydrogenation will take place via the limited number of reactive adsorbed hydrogen atoms. In our previous paper,<sup>2</sup> we concluded that the hydrogen atoms newly formed by adsorption are reactive but some of them remaining on the surface become stable with time.

We now discuss the results obtained at 300 s, where the time-variations of  $q_H$  and  $\Delta q_0$  are small.

(1) In region E,  $q_H$  approaches the value of  $s q_H$  with increasing of  $P_H$  as shown in fig. 10.  $\Delta q_0$  at 300 s, however, has a definite but very small value compared to that expected from the  $C_2H_4$  isotherm in fig. 5. This depression in  $\Delta q_0$  in region E supports the previous conclusion that ethylene diffusion is the rate-determining step.<sup>2</sup>

(2) In region H,  $\Delta q_0$  at 300 s approaches its saturation value, while  $q_H$  becomes extremely small (fig. 7).  $\Delta q_0$  at constant  $P_H$  (15.1 cmHg) depends on  $P_E$  as shown in fig. 5. Thus, in region H the surface is covered almost exclusively with ethylene and only a small portion with hydrogen atoms, supporting the conclusion that hydrogen diffusion is the rate-determining step.<sup>2</sup>

## POTENTIAL DETERMINING STEP

It has been reported that when a Pt electrode is brought into contact with  $C_2H_4$ , its open circuit potential is determined by the step <sup>1, 12, 15</sup>



In the present system, the electrode is in contact with both  $C_2H_4$  and  $H_2$ . In region H, the open circuit potential,  $V_r$ , 5 min after the introduction of a reaction gas is expressed as <sup>2</sup>

$$V_r \text{ (r.h.e.)/mV} = -60 \log (P_H/\text{cmHg}) + 100 \log (P_E/\text{cmHg}) + \text{const.} \quad (7)$$

Since the equilibrium condition of step (6) is given as

$$V_r \text{ (r.h.e.)} = \text{const.} - (RT/F) \ln a_{H(ads)}, \quad (8)$$

where  $a_{H(ads)}$  represents the activity of  $H(ads)$ , we obtain from eqn (7) and (8)

$$a_{H(ads)} = \text{const.} \times P_H \quad (9)$$

at a constant  $P_E$ . Comparison of eqn (9) with eqn (3) shows that the power of  $P_H$  is practically the same. Thus, we assume that the open circuit potential is determined by the equilibrium condition of step (6).

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