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# EXCHANGE REACTION BETWEEN ACETYLENE OR METHYLACETYLENE AND DEUTEROACETYLENE ON NICKEL

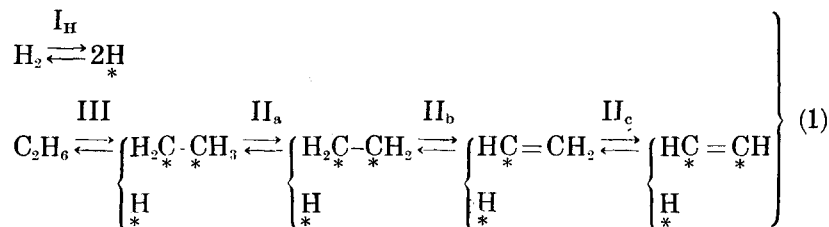
By

Koshiro MIYAHARA<sup>\*)</sup>

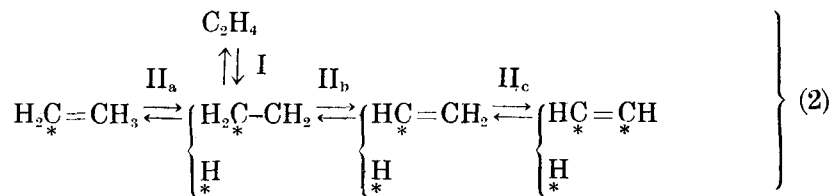
(Received June 28, 1957)

## § 1. Introduction

The present author<sup>1)</sup> has previously explained the experimental result of the exchange reaction between ethane and deuterium on various metal films observed by ANDERSON and KEMBALL<sup>2)</sup> on the basis of the reaction scheme



and that of the exchange and isomerization reaction of ethylene on nickel observed by FLANAGAN and RABINOVITCH<sup>3)</sup> similarly on the basis of the scheme<sup>4)</sup>

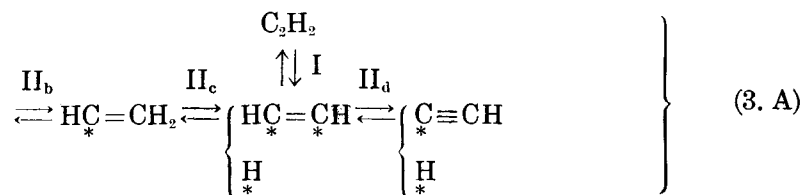


where H stands for protium P and deuterium D, \* signifies a bond with a chemisorption site and the parenthesized products, e. g.  $\left\{ \begin{array}{l} \text{H}_2\text{C}^*-\text{CH}_3 \\ \text{H}^* \end{array} \right\}$

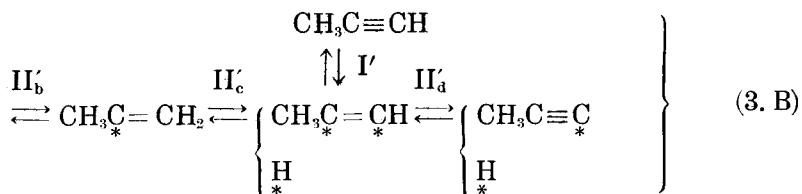
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are meant to be created from the products on their left, e. g.  $C_2H_6$ , to which the notation of the appropriate step, e. g. III is annexed. Experimental results have thus been quantitatively reproduced by adjusting the rate of each step of the schemes, assumed to be counterbalanced by its reversal, except that of  $II_c$  postulated instead quick enough to be practically in isotopic exchange equilibrium.

Step  $II_c$  may, on the other hand, give rise to such an exchange reaction as that between acetylene and deuterioacetylene observed by BOND, SHERIDAN and WHIFFEN,<sup>5)</sup> provided that  $H^*$  required for its occurrence were somehow secured, say, by the dissociation  $II_d$  of acetylene, as in the scheme,



where  $II_b$  and other steps implied in (1) and (2), which leads to hydrogenation products or  $H_2$ , are ignored because of their absence in the reaction product.<sup>5)</sup> The similar scheme might be advanced for the exchange reaction between methylacetylene and deuterioacetylene observed by the same group of authors<sup>7)</sup> with steps  $I'$  etc. respectively corresponding to  $I$  etc. as



where steps leading to the hydrogen exchange of methyl group of methylacetylene are excluded because of the observed absence of the relevant exchange product,<sup>7)</sup> and the possible alternative product  $\text{CH}_3\text{HC}=\text{CH}^*$  from  $\text{CH}_3\text{C}^*=\text{CH} + \text{H}^*$ , too, which just gives out the very  $H$  atom preliminarily picked up by  $\text{CH}_3\text{C}^*=\text{CH}$  contributing nothing to the exchange.

It is shown in the present paper that the above Schemes account for the experimental results of BOND *et al.*<sup>5)</sup> quantitatively by adjusting

*Exchange Reaction Between Acetylene or Methylacetylene on Nickel*

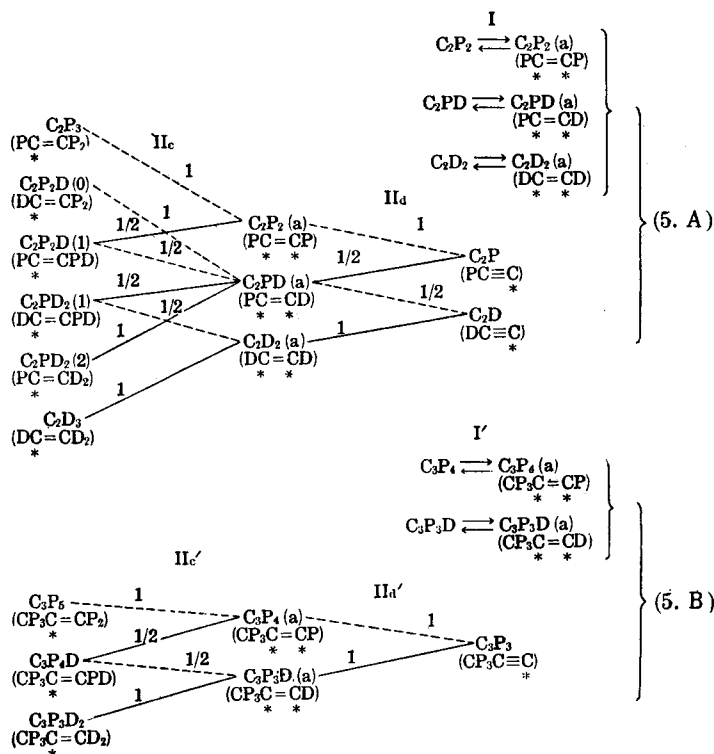
the ratio of the balanced rates  $V(j)$ 's ( $j=I, II_c, II_a$ ), and assuming that

$$V(j') = \lambda V(j) \quad (4)$$

where  $\lambda$  is a constant common to all  $j$ 's.

§ 2. Detailed Scheme and Rate Equations

Schemes (3.A) and (3.B) may be developed discriminating between P and D as



where the full structures of  $C_2P_2D(O)$ ,  $C_3P_5$  etc. are shown underneath respectively in the parenthesis; the dotted or full line denotes the transfer of P or D respectively, the annexed number the fraction of the rate of the dissociation specified by the line, of the atom group on its left side over the total rate of the dissociation of the same, identifying the kinetic behavior or P with that of D.

The rates  $V^{C_2P_2}$  etc. of formation of  $C_2P_2$  etc. may be expressed,

referring to the annexed number to the lines of (5. A) and (5. B) and denoting the fraction of  $C_2P_2$  etc. over the sum of those of the kindred atom groups differing only by isotopic or methyl substitution by  $y^{C_2P_2}$  etc. \*) , as

$$\left. \begin{aligned} V^{C_2P_2} &= V(I)(y^{C_2P_2(a)} - y^{C_2P_2}) \\ V^{C_2PD} &= V(I)(y^{C_2PD(a)} - y^{C_2PD}) \\ V^{C_2D_2} &= V(I)(y^{C_2D_2(a)} - y^{C_2D_2}) \end{aligned} \right\} \quad (6. A. 1)$$

for acetylenes  $C_2H_2$ 's in gas,

$$\left. \begin{aligned} V^{C_2P_2(a)} &= V(I)(y^{C_2P_2} - y^{C_2P_2(a)}) + V(II_c)(y^{C_2P_2} + \frac{1}{2}y^{C_2P_2D(1)} - y^{C_2P_2(a)}) \\ &\quad + V(II_d)(y^{C_2P}y^P - y^{C_2P_2(a)}) \\ V^{C_2PD(a)} &= V(I)(y^{C_2PD} - y^{C_2PD(a)}) + V(II_c)(y^{C_2P_2D(0)} + \frac{1}{2}y^{C_2P_2D(1)} \\ &\quad + \frac{1}{2}y^{C_2PD_2(1)} + y^{C_2PD_2(2)} - y^{C_2PD(a)}) + V(II_d)(y^{C_2P_2}y^P + y^{C_2D}y^P - y^{C_2PD(a)}) \\ V^{C_2D_2(a)} &= V(I)(y^{C_2D_2} - y^{C_2D_2(a)}) + V(II_c)(\frac{1}{2}y^{C_2PD_2(1)} + y^{C_2D_2} - y^{C_2D_2(a)}) \\ &\quad + V(II_d)(y^{C_2D}y^D - y^{C_2D_2(a)}) \end{aligned} \right\} \quad (6. A. 2)$$

for chemisorbed acetylenes  $C_2H_2(a)$ 's,

$$\left. \begin{aligned} V^{C_2P} &= V(II_d)(y^{C_2P_2(a)} + \frac{1}{2}y^{C_2PD(a)} - y^{C_2P}) \\ V^{C_2D} &= V(II_d)(\frac{1}{2}y^{C_2PD(a)} + y^{C_2D_2(a)} - y^{C_2D}) \end{aligned} \right\} \quad (6. A. 3)$$

for chemisorbed radicals  $HC \equiv C^*_$ 's,

$$\left. \begin{aligned} V^{C_2P_2} &= V(II_c)(y^{C_2P_2(a)}y^P - y^{C_2P_2}) \\ V^{C_2P_2D(0)} &= V(II_c)(\frac{1}{2}y^{C_2PD(a)}y^P - y^{C_2P_2D(0)}) \\ V^{C_2P_2D(1)} &= V(II_c)(y^{C_2P_2(a)}y^D + \frac{1}{2}y^{C_2PD(a)}y^P - y^{C_2P_2D(1)}) \\ V^{C_2PD_2(1)} &= V(II_c)(\frac{1}{2}y^{C_2PD(a)}y^D + y^{C_2D_2(a)}y^P - y^{C_2PD_2(1)}) \end{aligned} \right\} \quad (6. A. 4)$$

\*) The  $y^{C_2P_2}$ , for instance, is given as

$$y^{C_2P_2} = [C_2P_2] / \{ [C_2P_2] + [C_2PD] + [C_2D_2] + [C_3P_3] + [C_3PD] \}$$

where  $[C_2P_2]$  etc. denote the abundance of atom groups  $C_2P_2$  etc. respectively.

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$$\left. \begin{aligned} V^{C_2PD_2(2)} &= V(II_c) \left( \frac{1}{2} y^{C_2PD(a)} y^D - y^{C_2PD_2(2)} \right) \\ V^{C_2D_3} &= V(II_c) (y^{C_2D_2(a)} y^D - y^{C_2D_3}) \end{aligned} \right\}$$

for chemisorbed radicals  $HC_* = CH_2^*$ 's,

$$\left. \begin{aligned} V^{C_3P_4} &= V(I') (y^{C_3P_4(a)} - y^{C_3P_4}) \\ V^{C_3P_3D} &= V(I') (y^{C_3P_3D(a)} - y^{C_3P_3D}) \end{aligned} \right\} \quad (6. B. 1)$$

for methylacetylenes  $CP_3C \equiv CH$ 's in gas,

$$\left. \begin{aligned} V^{C_3P_4(a)} &= V(I') (y^{C_3P_4} - y^{C_3P_4(a)}) + V(II'_c) (y^{C_3P_4} + \frac{1}{2} y^{C_3P_4D} \\ &\quad - y^{C_3P_4(a)}) + V(II'_d) (y^{C_3P_3} y^P - y^{C_3P_4(a)}) \\ V^{C_3P_3D(a)} &= V(I') (y^{C_3P_3D} - y^{C_3P_3D(a)}) + V(II'_c) \left( \frac{1}{2} y^{C_3P_4D} + y^{C_3P_3D_2} \right. \\ &\quad \left. - y^{C_3P_3D(a)} \right) + V(II'_d) (y^{C_3P_3} y^D - y^{C_3P_3D(a)}) \end{aligned} \right\} \quad (6. B. 2)$$

for chemisorbed methylacetylenes  $CP_3C_* = CH^*$ 's,

$$V^{C_3P_3} = V(II'_d) (y^{C_3P_4(a)} + y^{C_3P_3D(a)} - y^{C_3P_3}) \quad (6. B. 3)$$

for chemisorbed radical  $CP_3C_* \equiv C_*$ ,

$$\left. \begin{aligned} V^{C_3P_3} &= V(II'_c) (y^{C_3P_4(a)} y^P - y^{C_3P_3}) \\ V^{C_3P_3D} &= V(II'_c) (y^{C_3P_4(a)} y^D + y^{C_3P_3D(a)} y^P - y^{C_3P_3D}) \\ V^{C_3P_3D_2} &= V(II'_c) (y^{C_3P_3D(a)} y^D - y^{C_3P_3D_2}) \end{aligned} \right\} \quad (6. B. 4)$$

for chemisorbed radicals  $CP_3C_* = CH_2^*$ 's, respectively. The  $y$ 's in above equations must satisfy, by definition, the relations

$$\left. \begin{aligned} y^P + y^D &= y^{C_2P_2} + y^{C_2PD} + y^{C_2D_2} + y^{C_3P_4} + y^{C_3P_3D} \\ &= y^{C_2P_2(a)} + y^{C_2PD(a)} + y^{C_2D_2(a)} + y^{C_3P_4(a)} + y^{C_3P_3D(a)} \\ &= y^{C_2P} + y^{C_2D} + y^{C_3P_3} \\ &= y^{C_2P_2} + y^{C_2P_2D(0)} + y^{C_2P_2D(1)} + y^{C_2PD_2(1)} + y^{C_2PD_2(2)} \\ &\quad + y^{C_2D_3} + y^{C_3P_3} + y^{C_3P_4D} + y^{C_3P_3D_2} = 1 \end{aligned} \right\} \quad (6. y)$$

**§ 3. Exchange Reaction Between Methylacetylene and Deuteroacetylene**

Specializing (6.A.1), ..., (6.B.4) to the initial condition of the reaction

$$y^{C_2D_2} = y^{C_2P_2} = 1/2, \quad y^{C_2P_2} = y^{C_2PD} = y^{C_3P_3D} = 0 \quad (7)$$

as well as to (4), and putting the rates  $V^{C_2P_2}$  etc. of intermediates  $C_2P_3(a)$  etc. individually to zero for the steady state,  $y^{C_2P_2(a)}$  etc. are solved as

$$\left. \begin{aligned} y^{C_2P_2(a)} &= \frac{\alpha(1-y^D)^2}{2(1+\alpha)(2+\alpha)}, \\ y^{C_2PD(a)} &= \frac{\alpha(1-y^D)(1+\alpha y^D)}{(1+\alpha)(2+\alpha)}, \\ y^{C_2D_2(a)} &= \frac{1+\alpha y^D y^{C_2PD(a)}}{2\{1+\alpha(1-y^D)\}}, \\ y^{C_3P_3(a)} &= \frac{1+\alpha(1-y^D)}{2(1+\alpha)}, \\ y^{C_3P_3D(a)} &= \frac{2y^D}{2(1+\alpha)} \end{aligned} \right\} \quad (8. y)$$

where

$$\alpha = \frac{\frac{V(II_c)}{2} + V(II_a)}{V(I)} \quad (8. \alpha)$$

The  $y^{C_2P_2(a)}$  etc. substituted from (8. y) into (6. A.1) or (6. B.1) give directly observable  $V^{C_2P_2}$  etc. or  $V^{C_2P_2}$  and  $V^{C_3P_3D}$  as the respective functions of  $y^D$ ,  $\alpha$  and  $\lambda$ . Parameters  $y^D$  and  $\alpha$  are first adjusted to the observed ratio  $V^{C_2P_2} : V^{C_2PD} : V^{C_2D_2}$  and then  $\lambda$  to the ratio  $V^{C_2PD} : V^{C_3P_3D}$  according to (6. y), (4) and (7) as shown in the Table.

TABLE: Initial relative rates of formation. Initial composition of gas: 49.5%  $CP_3C \equiv CP + 1\%$   $C_2PD + 49.5\%$   $C_2D_2$ , Catalyst: nickel, 62°C.

Parameters adjusted				Relative rates of formation in %					
Parameters	$y^D$	$\alpha$	$\lambda$	Remarks	Compounds				
					$CP_3C \equiv CP$	$C_2D_2$	$C_2PD$	$C_2P_2$	$CP_3C \equiv CD$
Adjusted values	0.70	6.36	0.68	obs.	53.	47.	40.	7.	53.
				calc.	50.8	49.2	42.0	7.2	50.8

The agreement of the observed and calculated values are quite satisfactory. It may be remarked that the values of  $\alpha$  and  $y^D$  are determined irrespective of the assumption of (4), as is evident from the above.

§ 4. Exchange Reaction Between Acetylene and Deuteroacetylene

On the basis of  $\alpha$ -value determined in the foregoing section, the experimental results of the subject will be accounted for in what follows.

We see from (8.  $\alpha$ ) and the  $\alpha$ -value given in the Table that either  $\text{II}_c$  or  $\text{II}_a$  must be appreciably quick compared with I.  $\text{II}_a$  may be taken slow enough because of the polymerization of acetylene, plausibly caused through  $\text{II}_a$ , not being observed in association with the present exchange reaction<sup>5)</sup> and  $\text{II}_b$ , too, because of the absence of the hydrogenation product<sup>5)</sup> as referred to in the introduction. The slowest steps of Scheme (3. A) are now  $\text{II}_b$  and  $\text{II}_a$ , while the exchange reaction between acetylene and deuteroacetylene is kept up by the two fast ones  $\text{II}_c$  and I, if once the steady concentration of H(a) is provided by  $\text{II}_a$ . The rates of steps in the present reaction are consequently of the relative magnitude

$$V(\text{II}_c) \gg V(\text{I}) \gg V(\text{II}_b) \text{ or } V(\text{II}_a). \quad (9)$$

Assuming now  $\text{II}_c$  quick enough to attain the isotopic exchange equilibrium,  $y^{\text{C}_2\text{PD(a)}}$  is given as

$$y^{\text{C}_2\text{PD(a)}} = 2y^{\text{P}} y^{\text{D}}. \quad (10. y. 1)$$

For 1:1 mixture of acetylene and deuteroacetylene we have on the other hand

$$y^{\text{P}} = y^{\text{D}} = 1/2 \quad (10. y. 2)$$

on account of the assumed identity of the kinetic behavior of P with that of D, and hence according to (6.A.1), (10.y.1) and (10.y.2)

$$V^{\text{C}_2\text{PD}} = d(Py^{\text{C}_2\text{PD}})/dt = V(\text{I})(1 - 2y^{\text{C}_2\text{PD}})/2, \quad (11. a)$$

provided that  $V(\text{I})$  is measured by the corresponding increasing rate of the partial pressure, or by integration at constant total pressure  $P$ ,

$$1 - 2y^{\text{C}_2\text{PD}} = \exp[-V(\text{I})t/P] \quad (11. b)$$

where  $t$  is the time.

Eq. (11. b) is in good agreement with the observation of BOND *et al.* for the exchange reaction of 1:1 mixture of  $\text{C}_2\text{P}_2$  and  $\text{C}_2\text{D}_2$  on nickel at 119°C as shown in Fig. 1, from which  $V(\text{I})/P$  is determined at  $2.05 \times 10^{-2} \text{ min}^{-1}$ .

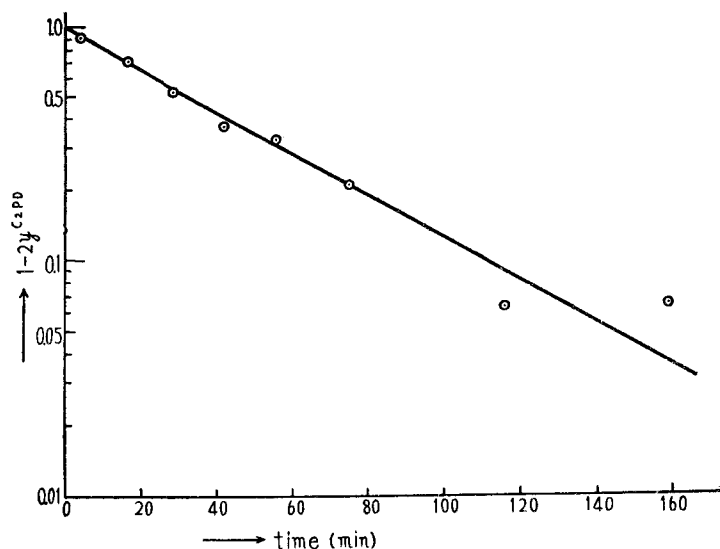
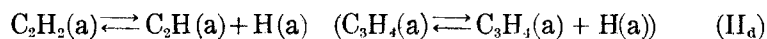
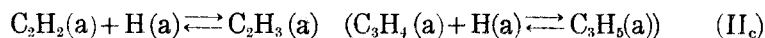
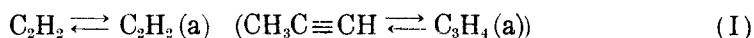


Fig. 1. Observed fraction  $y_{C_2PD}^{C_2D_2}$  of  $C_2PD$  formed from 1:1 mixture of  $C_2P_2$  and  $C_2D_2$ . Catalyst: nickel, 119°C.

### § 5. Discussion

The present analysis has verified the mechanism of the exchange reaction between deuterioacetylene and acetylene or methyl-acetylene given by (3.A) and (3.B) respectively, i. e.



H(a): chemisorbed hydrogen atom,

where  $II_c$  is quick enough to attain the isotopic exchange equilibrium.

BOND *et al.*<sup>5)</sup> proposed a bimolecular mechanism for the reaction, with which hydrogen atoms are interchanged between a chemisorbed and a physically adsorbed acetylene molecule, on the ground of the experimental facts, i. e.

i) The observed formation rate of  $C_2PD$  from 1:1 mixture of acetylene and deuterioacetylene obeys approximately the rate equation

$$dP_{C_2PD}/dt \propto 3.2 P_{C_2P_2} P_{C_2D_2} - P_{C_2PD}^2 \quad (12. a)$$

at constant total pressure  $P$ , where  $P_{C_2PD}$  etc. represent the partial

pressures of C<sub>2</sub>PD etc. respectively, whereas the  $\frac{dP_{C_2PD}}{dt}$  at the initial stage of the exchange reaction varied with  $P$  as

$$dP_{C_2PD}/dt \propto P^{0.65} \quad (12. b)$$

ii) Hydrogenation of acetylene proceeds in the presence of nickel as

$$-dP/dt = k' P_{H_2}^1 P_{C_2H_2}^0 \quad (13)$$

where  $k'$  is the rate constant.

iii) The conversion of para-hydrogen is strongly inhibited by acetylene.

iv) Hydrogenation or polymerization of acetylene was not observed in association with the present exchange reaction.

These facts are alternatively accounted for on the basis of the present mechanism as follows respectively under the same headings.

i) Eq. (12. a) may be written in the form

$$dy^{C_2PD}/dt = k \left\{ 3.2 y^{C_2P_2} y^{C_2D_2} - (y^{C_2PD})^2 \right\}$$

remembering the relations  $P_{C_2PD} = P y^{C_2PD}$  etc., where  $k$  is a constant at constant total pressure. There exists, however, for 1:1 mixture of acetylene and deuterioacetylene, a stoichiometric relation

$$y^{C_2P_2} = y^{C_2D_2} = (1 - y^{C_2PD})/2.$$

We have now from the above two relations

$$dy^{C_2PD}/dt = k \left( \frac{\sqrt{3.2}}{2} - \frac{\sqrt{3.2}}{2} y^{C_2PD} + y^{C_2PD} \right) \left( \frac{\sqrt{3.2}}{2} - \frac{\sqrt{3.2}}{2} y^{C_2PD} - y^{C_2PD} \right)$$

i. e.

$$dy^{C_2PD}/dt = 0.8 k (1 + 0.117 y^{C_2PD})(1 - 2.12 y^{C_2PD})$$

which is almost identical with (11. a), the coefficient of  $y^{C_2PD}$  in the last factor  $(1 - 2.12 y^{C_2PD})$  of the above equation being different from that of the varying factor of (11. a) only by 6%, whereas the other  $(1 + 0.117 y^{C_2PD})$  increasing from 1 to less than 1.06, as  $y^{C_2PD}$  increases from 0 to less than 0.5.

The exact validity of (11. a) demonstrated in Fig. 1 accounts thus for the "bimolecular" kinetics of (12. a) at least approximately.

The experimental fact of (12. b) is, on the other hand, qualitatively interpreted as below. At the initial stage of the reaction, when  $y^{C_2PD} = 0$ ,  $V^{C_2PD}$  may be expressed, according to (11. a) as

$$V^{C_2PD} = 2V(I) y^P y^D = V(I)/2 .$$

and hence we have

$$(\partial \ln V^{C_2PD} / \partial \ln P)_T = (\partial \ln V(I) / \partial \ln P)_T \quad (14)$$

i. e. the pressure dependence of the formation rate of  $C_2PD$  is equal to that of balanced forward or backward rate of the acetylene chemisorption.

It has been shown by HORIUTI *et al.*<sup>(6)\*</sup> that the rate of chemisorption  $V(I_H)$  of hydrogen molecule, which requires two unoccupied adjacent sites of chemisorption similarly as acetylene molecule does, varies with the pressure  $P_{H_2}$  of hydrogen in equilibrium with chemisorbed hydrogen atoms, as

$$(\partial \ln V(I_H) / \partial \ln P_{H_2})_T = (\alpha) / 2 \quad (15)$$

allowing both for the variation of the fraction of unoccupied sites available for the chemisorption and the repulsive interaction between the critical complex of chemisorption and chemisorbed hydrogen atoms, where  $(\alpha)$  decreases from 2 to 0 along with the increasing coverage of the catalyst's surface with hydrogen from 0 to 1.<sup>7)</sup>

Assuming similar variation of the available fraction of chemisorption sites and repulsive interactions,  $(\partial \ln V^{C_2PD}) / (\partial \ln P)_T$  of the present reaction may be positive and smaller than unity as in the case of (15) in accordance with the observed result of (12. b).

\*) HORIUTI *et al.* [Ref. 7] have explained the well-known TAFEL's law,

$$\ln i = - \frac{(\alpha) FE}{RT} + \text{Const.} \quad (\alpha) \cong 0.5: \text{TAFEL's constant, F: Faraday} \quad (i)$$

of hydrogen electrode process, with the allowance referred to in the text on basis of the catalytic mechanism, in which the recombination of  $H(a)$  determines the rate;  $i$  is the forward rate per unit area in terms of the electricity conveyed, i. e. the appropriate current density and  $E$  the electrode potential. At the NERNST's equilibrium we have

$$FE = \frac{RT}{2} \ln P_{H_2} + \text{Const.} \quad (ii)$$

and hence, eliminating  $FE$  from (i) and (ii) and replacing  $i$  by the forward rate  $V(I_H)$  of the rate-determining step at equilibrium,

$$\ln V(I_H) = (\alpha) \frac{\ln P_{H_2}}{2} + \text{Const.}$$

Eq. (i) and hence (ii) follow from the picture of the catalytic mechanism as experimentally verified, quite irrespective of the presence of the solution,  $E$  just giving a measure of the chemical potential of  $H(a)$ , which uniquely determines the rate of the controlling step. It follows then that the above equation and hence (15) in the text hold for the simple chemisorption of hydrogen irrespective of the absence of the solution.

ii) It has previously been concluded with regard to the Scheme (1) of the exchange reaction between ethane and deuterium that

$$V(\text{II}_c) \gg V(\text{II}_a) > V(\text{III}) \cong V(\text{II}_b) \gg V(\text{I}_H), \quad (16)$$

i. e. that all steps of H(a)-addition in the course of hydrogenation of acetylene to ethane are far quicker than the chemisorption  $\text{I}_H$  of hydrogen molecule, i. e., the process of H(a)-formation.

The experimental condition of acetylene hydrogenation is now brought about by replacing ethane of the above exchange reaction with acetylene. All steps of H(a)-addition are quickened irreversibly at the moment of the replacement when H(a)-concentration is still that of the former steady state, whereas  $\text{I}_H$  remains unchanged or is even retarded, if chemisorbed acetylene or hydrogenated acetylene repulses the critical complex of the chemisorption of hydrogen molecule similarly as in the case of i). The new steady state is now attained as H(a)-concentration is sufficiently reduced for the respective steps of H(a)-addition to match the fixed or even diminished rate of H(a)-formation of  $\text{I}_H$ .  $\text{I}_H$  remains thus as the rate-determining step at the steady state of the acetylene hydrogenation.

The experimental condition of the acetylene-deuteroacetylene exchange is now derived from the latter by reducing the hydrogen pressure. The forward rate of  $\text{I}_H$  will thus be reduced in proportion to the hydrogen pressure, the state of chemisorption, on which the interaction between the critical complex of  $\text{I}_H$  and adsorptives depends, having less to do with the hydrogen pressure because of the rate-determining step of  $\text{I}_H$ .\*) The rate of H(a)-additions will however

\*) The rate  $\bar{v}$  of a thermal step, homogeneous or heterogeneous, is given [HORIUTI, this Journal 1, 8 (1948), § 23] as

$$\bar{v} = \kappa \frac{kT}{h} \frac{p^*}{p^I}, \quad (i)$$

where  $\kappa$  is the transmission coefficient,  $k$  or  $h$  the BOLTZMANN's or PLANCK's constant,  $T$  the absolute temperature and  $p^*$  or  $p^I$  the BOLTZMANN factor of the chemical potential of the critical or initial complex respectively. The chemical potential of the critical complex or  $p^*$  of the heterogeneous step  $\text{I}_H$  depends now on the state of chemisorption of the catalyst's surface; since the latter state is practically independent of  $P_H$ , the same must be true with  $p^*$ .

The  $\bar{v}$  of  $\text{I}_H$  must now according to (i) be inversely proportional to  $p^I$  of  $\text{I}_H$ . We have  $p^I = Q^{\text{H}_2} / N^{\text{H}_2}$  [HORIUTI, *ibid.*, § 5] for the initial complex of  $\text{I}_H$ , i. e., hydrogen molecule in gas, where  $Q^{\text{H}_2}$  is the partition function of a hydrogen molecule in unit volume and  $N^{\text{H}_2}$  its concentration in gas. The  $\bar{v}$  of  $\text{I}_H$  and hence the overall rate of acetylene hydrogenation controlled by  $\text{I}_H$  must be proportional to  $N^{\text{H}_2}$  or to  $P_H$ ,  $Q^{\text{H}_2}$  being constant at constant temperature.

hardly be affected because of their partial equilibrium approximately attained at the steady state on account of the sufficiently slow rate-determining step of  $I_H$ . The rate-determining step of  $I_H$  is in consequence even the more assured by reducing hydrogen pressure. It follows that, when the condition of the acetylene exchange dealt with in the present paper, i. e. the state of balanced forward and backward rates of all steps is finally attained,  $I_H$  must be slowest. The relative magnitude  $V(II_c) \gg V(II_b)$  of (16) holds now *a fortiori* in the present case, when acetylene is present alone without hydrogen, inasmuch as  $V(II_b)/V(II_c)$  should decrease with decreasing H(a)-concentration. These conclusions arrived at are completely in conformity with the result (9) of the present analysis, where  $V(I_H)$  is imperceptibly small as referred to in the introduction. The first order dependence of the rate of acetylene hydrogenation on  $P_{H_2}$ , as well as the zero order dependence on  $P_{C_2H_2}$ , follows immediately from the rate-determining step of  $I_H$  in accordance with the above consideration.

iii) Acetylene is hydrogenated with a rate determined by  $I_H$  as detailed in ii), which means an appreciable reduction of H(a)-concentration and hence of the backward rate of  $I_H$  due to the presence of acetylene compared with in the case of hydrogen present alone in contact with the catalyst i. e. a strong inhibition of para-hydrogen conversion by acetylene.

iv) Relation (9), concluded in § 4 on the basis of the present analysis is thus consistent with the fact iv) besides with the other facts i), ii) and iii), as discussed above.

It might further be remarked in conclusion that the exchange reaction between  $C_2P_4$  and  $C_2D_4$  on nickel was observed by FLANAGAN and RABINOVITCH<sup>3)</sup> in accordance with the present scheme but in deviation from the view of BOND *et al.*,<sup>5)</sup> who refers plausibly to the absence of this exchange in accordance with their mechanism. It is now expected that the exchange reaction between  $C_2D_2$  and  $C_2P_4$  on nickel similarly proceeds according to the Schemes (2) and (3.A) and that the relative magnitudes of the rates given in (16) and (9) as well as the rate of ethylene chemisorption is more closely determined from the analysis of this sort of exchange reactions.

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*Exchange Reaction Between Acetylene or Methylacetylene on Nickel*

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