<table>
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<tr>
<th>Title</th>
<th>FINE STRUCTURE OF REACTION BETWEEN ETHANE AND DEUTERIUM ON VARIOUS EVAPORATED METAL FILMS: EXPLANATION TO ANDERSON AND KEMBALL'S EXPERIMENT</th>
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<td>Author(s)</td>
<td>MIYAHARA, Koshiro</td>
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FINE STRUCTURE OF REACTION BETWEEN
ETHANE AND DEUTERIUM ON
VARIOUS EVAPORATED METAL FILMS

Explanation to ANDERSON and KEMBALL's Experiment

By

Koshiro MIYAHARA

(Received June 28, 1956)

Introduction

ANDERSON and KEMBALL have recently observed the catalytic deuteration of ethane on various evaporated metal films by means of a mass-spectrometer, determining the relative abundances of different deuteroethanes at the initial stage of the reaction. They tried to explain the experimental results although not very consistently.

The experimental results are explained in the present paper in accordance with the 'structure theory' of HORIUTI, developed with special reference to the hydrogenation of ethylene in extension of the mechanism of HORIUTI and POLANYI, by the similar method to that the 'fine structure theory' of KEN, who analysed the catalytic deuteration of ethylene and propylene.

Reaction Mechanism and Fine Structure Calculation

The hydrogenation and simultaneous hydrogen-exchange proceed by the scheme

\[
\begin{align*}
\ce{C_2H_4 &<-> CH_2-CH_2}^* & \text{II} & \ce{CH_3-CH_2}^* \\
\text{I} & \text{(below optimum temp.)} & \text{III} & \ce{C_2H_6} \\
\ce{CH_3-CH_2}^* & \text{II} & \ce{CH_3-CH_2}^* \\
\ce{CH_3-CH_2}^* & \text{III} & \ce{C_2H_6} \\
\end{align*}
\]

according to the structure theory, the rate of hydrogenation being controlled by I or III respectively below or above the optimum temperature, where * denotes a chemisorption site and H stands for protium.

*) Department of Chemistry, Faculty of Science, Hokkaido University.
(P) or deuterium (D).

The scheme (1) might be supplemented as

\[
\begin{align*}
\text{III} & \rightarrow \begin{cases} 
\text{H}^* \\
\text{CH}_2-\text{CH}_3 \\
\text{CH} = \text{CH}_2
\end{cases} \\
\text{II}^a & \rightarrow \begin{cases} 
\text{H}^* \\
\text{CH}_2-\text{CH}_3 \\
\text{CH} = \text{CH}_2
\end{cases} \\
\text{II}^b & \rightarrow \begin{cases} 
\text{H}^* \\
\text{CH}_2-\text{CH}_3 \\
\text{CH} = \text{CH}_2
\end{cases} \\
\text{II}^c & \rightarrow \begin{cases} 
\text{H}^* \\
\text{CH}_2-\text{CH}_3 \\
\text{CH} = \text{CH}_2
\end{cases}
\end{align*}
\]

(2)

\[\text{H}_2 \rightarrow 2\text{H} \]

with regard to hydrocarbon intermediates in accordance with the experimental facts of the self-hydrogenation of ethylene and of the hydrogen-exchange between light and deuterated ethylene observed on some metallic catalysts\(^7\),\(^9\). The intermediate \(\text{C}_2\text{H}_3\) has been proposed by Farkas\(^8\) with reference to his dissociative mechanism, whereas \(\text{CH} = \text{CH}\) or the 'acetylenic complex' by Beck\(^9\) to account for the catalytic poison on the basis of the composition of the chemisorbed ethylene. This scheme is detailed with distinction between protium and deuterium as

\[
\text{d} \rightarrow \begin{cases} 
\text{III}^a \\
\text{II}^b \\
\text{II}^c
\end{cases} \\
\text{C}_2\text{P}_3 \\
\text{C}_2\text{P}_4 \\
\text{C}_2\text{P}_5
\end{cases}
\]

(3)
where $d_n$ denotes a $n$-th deuterated ethane molecule and dotted or full line the step in which P or D respectively is either released or picked up. The increasing rate $\dot{Y}^{d_n}$ etc. of respective deutero-compound $d_n$ etc. can be expressed as

$$
\begin{align*}
\dot{Y}^{P_d} &= v(I) [(y_P^D - y_P^P)] \\
\dot{Y}^{P_D} &= v(I) [2y_P^P - y_P^P] \\
\dot{Y}^{P_i} &= v(I) [(y_P^P - y_P^P)] 
\end{align*}
$$

(4)

for hydrogen in gas,

$$
\begin{align*}
\dot{Y}^{d_n} &= v(III) (y_0^P y_D - y_0^P) \\
\dot{Y}^{d_n} &= v(III) (y_0^P y_D + y_0^P y_D - y_0^P y_D) \\
\dot{Y}^{d_n} &= v(III) (y_0^P y_D - y_0^P)
\end{align*}
$$

(5)

for ethanes in gas,

$$
\begin{align*}
\dot{Y}^{c,P_D} &= v(II_a) (y_c^P y_D - y_c^P y_D) + v(III) \left( \frac{1}{6} y_c^P + y_c^P - y_c^P y_D \right) \\
\dot{Y}^{c,P_D} &= v(II_a) (y_c^P y_D + y_c^P y_D - y_c^P y_D) + v(III) \left( \frac{1}{3} y_c^P - y_c^P - y_c^P y_D \right) \\
\dot{Y}^{c,P_D} &= v(II_a) \left( \frac{1}{6} y_c^P + y_c^P + y_c^P y_D \right)
\end{align*}
$$

(6)

for adsorbed ethyl radicals,

$$
\begin{align*}
\dot{Y}^{c,P_D} &= v(II_a) \left( y_c^P y_D + \frac{1}{6} y_c^P y_D - y_c^P y_D \right) + v(II_b) (y_c^P y_D + y_c^P y_D - y_c^P y_D) \\
\dot{Y}^{c,P_D} &= v(II_a) \left( \frac{5}{6} y_c^P y_D + \frac{1}{3} y_c^P y_D - y_c^P y_D \right) + v(II_b) (y_c^P y_D + y_c^P y_D - y_c^P y_D) \\
\dot{Y}^{c,P_D} &= v(II_b) \left( \frac{1}{6} y_c^P y_D + y_c^P y_D - y_c^P y_D \right)
\end{align*}
$$

(7)

for adsorbed ethylenes,

$$
\begin{align*}
\dot{Y}^{c,P_D} &= v(II_b) \left( y_c^P y_D + \frac{1}{4} y_c^P y_D - y_c^P y_D \right) + v(II_c) (y_c^P y_D + y_c^P y_D - y_c^P y_D) \\
\dot{Y}^{c,P_D} &= v(II_b) \left( \frac{3}{4} y_c^P y_D + \frac{1}{2} y_c^P y_D - y_c^P y_D \right) + v(II_c) (y_c^P y_D + y_c^P y_D - y_c^P y_D) \\
\dot{Y}^{c,P_D} &= v(II_b) \left( \frac{1}{4} y_c^P y_D + y_c^P y_D - y_c^P y_D \right)
\end{align*}
$$

(8)
for C₃H₅'s and

\[
\begin{align*}
\dot{Y}^{c,p_1} &= v(IIc) \left( y^{c,p_1} + \frac{1}{4} y^{c,p_1,p} - y^{p_1} \right) \\
\dot{Y}^{c,p_2} &= \ldots \\
\dot{Y}^{c,p_3} &= \ldots
\end{align*}
\]

for acetylenic complexes respectively.

In above equations, \( y^j \) is the fraction of the number of \( j \)-th deuterated product \( (\delta_j) \) over the total number of the product regardless of isotopes \( (\delta) \), \( v(j) \) the forward rate of the \( j \)-th step of scheme (2) at equilibrium balanced each other, and the coefficient of each \( y \)'s the probability of forward transition of relevant step of scheme (3) with due regard to the configurational isomers for each product, e.g. CP₂-CPD₂, CPD-CPD and CD₂-CP for CP₂D₂.

Imposing on these equations the initial condition of the reaction as \( y^{p_1} = y^{d*} = 1 \) and \( y^{p_d} = y^{p_n} = y^{p} = \ldots = y^{p_4} = 0 \), and the steady state condition with respect to every intermediate, we have

\[
\begin{align*}
\dot{Y}^{d_0} &= v(III) (y^{c,p,p'} - y^{n}) \\
\dot{Y}^{d_1} &= v(III) (y^{c,p,p_1} - y^{d_1} + y^{c,p_1,p} y^{p}) \\
( \ell : & \text{ an integer of } 1 \leq \ell \leq 6 )
\end{align*}
\]

\[
\begin{align*}
a_0y^{c,p_1} &= c_0y^{c,p_1,p} + e_0 \\
a_my^{c,p_1} - m_p m_p' &= b_my^{c,p_1} - m_p m_p' + c_my^{p_1} - m_p m_p' + e_m \\
( m : & \text{ an integer of } 1 \leq m \leq 5 )
\end{align*}
\]

and

\[
\begin{align*}
(1 + ry^p) y^{c,p_1} &= y^{c,p_1} + \frac{1}{4} y^{c,p_1,p} + \ \frac{y^p}{4} y^{c,p_1,p} \\
\left(1 + \frac{r}{4} + \frac{y^p}{2} \right) y^{c,p_1,p} &= \frac{3}{4} y^{c,p_1,p} + \frac{1}{2} y^{c,p_1,p} + \frac{y^p}{4} y^{c,p_1,p} + \gamma \left( \frac{3}{4} y^{c,p_1,p} + \frac{y^p}{4} y^{c,p_1,p} \right) \\
\left(1 + \frac{3r}{4} y^p \right) y^{c,p_1} &= \frac{1}{2} y^{c,p_1} + \frac{3}{4} y^{c,p_1} + \gamma \left( \frac{3}{4} y^{c,p_1} + \frac{y^p}{4} y^{c,p_1} \right) \\
(1 + ry^p) y^{p_1} &= \frac{1}{4} y^{c,p_1} + y^{c,p_1} + \gamma y^p y^{c,p_1}
\end{align*}
\]

where
Fine Structure of Reaction Between Ethane and Deuterium

\[
\begin{align*}
\alpha_0 &= \beta + y^D \\
\alpha_1 &= \frac{1 + \beta - \frac{5}{6} + \frac{2}{3} y^D}{\alpha} \\
\alpha_2 &= \frac{1 + \beta - \frac{2}{3} + \frac{1}{3} y^D}{\alpha} \\
\alpha_3 &= \frac{1 + \beta - \frac{1}{3} - \frac{1}{3} y^D}{\alpha} \\
\alpha_4 &= \frac{1 + \beta - \frac{1}{3} - \frac{2}{3} y^D}{\alpha} \\
\alpha_5 &= \frac{1 + \beta - y^D}{\alpha}
\end{align*}
\]

\[
\begin{align*}
b_0 &= 1 \\
b_1 &= \frac{1}{3} y^D \\
b_2 &= \frac{5}{6} y^D \\
b_3 &= \frac{2}{3} y^D \\
b_4 &= \frac{1}{3} y^D \\
b_5 &= \frac{1}{6} y^D
\end{align*}
\]

\[
\begin{align*}
c_0 &= \frac{1}{6} y^D \\
c_1 &= \frac{1}{3} y^D \\
c_2 &= \frac{2}{3} y^D \\
c_3 &= \frac{5}{6} y^D \\
c_4 &= y^D = 1 - y^D
\end{align*}
\]

\[
e_0 = \frac{(1-a)(1 + \beta)}{\alpha} + \beta(y^D)\gamma^D y^P, \\
e_1 = \beta[2y^D y^D y^D y^D + (y^D) y^P y^D y^D y^D] \\
e_2 = \beta[(y^D) y^D y^D y^D + 2y^D y^D y^D y^D + (y^D) y^D y^D y^D] \\
e_3 = \ldots \\
e_4 = \ldots \\
e_5 = \beta(y^D)\gamma^D y^P
\]

\[
A_\alpha = \frac{v(II_a)}{v(II_a) + v(III)} , \quad \beta = \frac{v(II_b)}{v(II_a)} \text{ and } \gamma = \frac{v(II_c)}{v(II_b)} . \quad (13)
\]

The initial rates of formation of respective ethane could be, in principle, calculated by eliminating \(y^D y^P\), etc., \(y^D y^P\), etc. and \(y^D y^P\), etc. from Eqs. (10), (11) and (12). The laborious calculation might be avoided by assuming that step IIc is isotopically equilibrium. The \(y^D y^P\), etc. are then respectively expressed as \(y^D y^P = n (y^D)^n (1 - y^P)^n\) \((n): an \text{ integer of } 0 \leq n \leq 3 \text{ and } \sum_{n=0}^{3} y^D y^P = 1\).

Eq. (11) is now solved as

\[
\begin{align*}
y^D y^P &= A_0 B_0 \\
y^D y^P - m B_m &= A_m B^D y^D - m B_{m-1} + B_m \quad (1 \leq m \leq 5)
\end{align*}
\]

where

\[
A_0 = \frac{b_0}{\alpha_0}, \quad A_{0-m} = \frac{b_{0-m}}{\alpha_{0-m} - c_{0-m} A_{0-m}}
\]

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It follows from (10) and (14)

\[
\begin{align*}
\dot{Y}^{a_d} &= y^P v(III) \left( y^{C_2P_1} - \frac{1}{y^P} \right) \\
\dot{Y}^{a_m} &= y^P v(III) \left[ y^{C_2P_1} - m P_{m-1} y^D (\mathcal{Q} + A_m) + B_m \right] \\
\dot{Y}^{a_t} &= y^P v(III) y^{C_2D_{t}} \mathcal{Q} \quad (1 \leq m \leq 5)
\end{align*}
\]

where

\[
\mathcal{Q} = \frac{y^D}{y^P}.
\]

The ratio of \( \dot{Y}^{a_d}, \dot{Y}^{a_m}, \ldots \) and \( \dot{Y}^{a_t} \) gives the distribution of deuterioethanes itself in the initial stage of the reaction. Table compares the observed distribution with values evaluated by Eq. (15) with a suitable choice of values of \( \alpha, \beta \) and \( y^D \) (or \( \mathcal{Q} \)). The agreement is quite satisfactory.

**Discussions**

1. If \( \beta = 0 \), namely, if the hydrocarbon intermediates were adsorbed ethyl and ethylene similarly as in the case of assoiactive mechanism or Anderson and Kembhavi's explanation, a distribution with minimum which is actually observed with Pt and other catalysts can not be theoretically reproduced. The existence of dissociated ethylenes is hence necessary in general.

2. The last four columns of the Table show the relative magnitude of rates of steps involved in scheme (2) and the slowest one calculated on the basis of the above analysis as below.

The conditions of the steady state are given by scheme (3) and the initial conditions for the reaction as

\[
y^P [2v(I)+v(IIa)+v(IIb)+v(III)] = v(II) \left( y^{C_2P_1} + \ldots + \frac{1}{6} y^{C_2P_{1D}} \right) + v(IIb) \left( y^{C_2P_1} + \ldots + \frac{1}{4} y^{C_2P_{2D}} \right) + v(III)
\]

for \( P \) and

\[
y^D [2v(I)+v(IIa)+v(IIb)+v(III)] = 2v(I) + v(II) \left( \frac{1}{6} y^{C_2P_{1D}} + \ldots + y^{C_2P_{3D}} \right) + v(IIb) \left( \frac{1}{4} y^{C_2P_{2D}} + \ldots + y^{C_2P_{3D}} \right)
\]

for \( D \) respectively. From these two conditions and Eq. (16) we have
### Observed and Theoretical Distributions of Deuteroethanes

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Temp. °C</th>
<th>Deuteroethane %</th>
<th>y^D</th>
<th>α</th>
<th>β</th>
<th>1-α/α</th>
<th>ε</th>
<th>Slowest Step.</th>
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<tr>
<td></td>
<td></td>
<td>d_1   d_2   d_3   d_4   d_5   d_6</td>
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<td></td>
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<tr>
<td>W</td>
<td>-80 ~ -29</td>
<td>obs. 78  12  5.1  2.0  9.0  0.6</td>
<td>0.30</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.45</td>
<td>I</td>
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<td></td>
<td></td>
<td>calc. 78  122 4.7  3.8  1.0  0.0</td>
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<td></td>
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<tr>
<td>Mo</td>
<td>-50 ~ 0</td>
<td>obs. 81  14  3.0  0.7  0.0  0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>calc. 81  15  3.1  0.6  0.0  0.0</td>
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<td></td>
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<tr>
<td>Ta</td>
<td>-50 ~ 0</td>
<td>obs. 81  15  3.1  0.6  0.0  0.0</td>
<td>0.20</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>0.09</td>
<td>I</td>
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<td></td>
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<td>calc. 81  15  3.1  0.6  0.0  0.0</td>
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<tr>
<td>Ni (orient)</td>
<td>0 ~ 75</td>
<td>obs. 90  10  0.0  0.0  0.0  0.0</td>
<td>0.05</td>
<td>0.6</td>
<td>0.6</td>
<td>0.67</td>
<td>0.23</td>
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<td>calc. 90.6 8.6  0.8  0.0  0.0  0.0</td>
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<tr>
<td>Ni</td>
<td>0 ~ 75</td>
<td>obs. 88  8.5  0.0  0.0  0.6  3.0</td>
<td>0.99</td>
<td>0.2</td>
<td>1.0</td>
<td>4.0</td>
<td>269.</td>
<td>II_a (= II_b)</td>
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<tr>
<td></td>
<td></td>
<td>calc. 88  8.5  0.0  0.0  0.1  2.4</td>
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<tr>
<td></td>
<td>162 ~ 195</td>
<td>obs. 40  10  4.0  5.0  10.0 30.0</td>
<td>0.92</td>
<td>0.65</td>
<td>1.0</td>
<td>0.54</td>
<td>8.0</td>
<td>III</td>
</tr>
<tr>
<td></td>
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<td>calc. 43 13  3.8  2.3  10.1 27.4</td>
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<tr>
<td>Zr</td>
<td>158 ~ 192</td>
<td>obs. 52  17  5.1  4.3  7.0 14.0</td>
<td>0.90</td>
<td>0.55</td>
<td>0.7</td>
<td>0.82</td>
<td>8.1</td>
<td>III (≈ II_b)</td>
</tr>
<tr>
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<td>calc. 54.4 17.1 4.9  2.3  5.6 15.7</td>
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<tr>
<td>Cr</td>
<td>149 ~ 215</td>
<td>obs. 47  18  6.6  6.0  7.2 15.0</td>
<td>0.96</td>
<td>0.6</td>
<td>0.5</td>
<td>0.67</td>
<td>15.7</td>
<td>III (≈ II_b)</td>
</tr>
<tr>
<td>V</td>
<td>102 ~ 210</td>
<td>obs. 46  19  5.7  5.1  7.5 16.0</td>
<td></td>
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<td></td>
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<td>calc. 46.9 19.4 7.2  2.8  5.0 18.8</td>
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<tr>
<td>Pt</td>
<td>134 ~ 192</td>
<td>obs. 19  17  12  10  5.0 25.0</td>
<td>0.90</td>
<td>0.83</td>
<td>0.1</td>
<td>0.205</td>
<td>3.1</td>
<td>III (≈ II_b)</td>
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<td>calc. 19.4 16.5 14.2 14.3 15.0 20.5</td>
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<tr>
<td>Pd</td>
<td>145 ~ 207</td>
<td>obs. 5  6.4  5.2  8.2  9.3 21.7</td>
<td>0.95</td>
<td>0.99</td>
<td>0.1</td>
<td>0.01</td>
<td>1.14</td>
<td>III</td>
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<tr>
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<td>calc. 4.2  4.5  5.2  8.2  9.3 21.7</td>
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</table>
\[
\frac{v(I)}{v(II)} = \frac{1}{2} \left[ \frac{1-a}{a} + D' \right] = \delta
\]

where
\[
D = \sum_{m=1}^{5} f_m y^c P_{m-1}^m + f_6 (1-y^3) y^c P_5,
\]
\[
D' = \sum_{m=1}^{5} f_m y^c P_{m-1}^m + f_6 (1-y^3) y^c P_5,
\]

\[
f_1 = \frac{4+9\beta}{24(1+\beta)}, \quad f_2 = \frac{4+7\beta}{12(1+\beta)}, \quad f_3 = \frac{8+15\beta}{12(1+\beta)}, \quad f_4 = \frac{20+39\beta}{24(1+\beta)},
\]

\[
f_5 = \frac{1+2\beta}{1+\beta} \quad \text{and} \quad f_6 = \frac{\beta^2}{1+\beta}.
\]

The relative rates of four steps are given by Eqs. (13) and (17) as
\[
v(I) : v(II) : v(III) = \delta : 1 : 13 : \frac{1-a}{a}.
\]

It is seen from Table that the values of parameters \(a\) and \(\delta\) of nickel at lower temperature are extraordinary compared with those of other catalysts. For these values are responsible the non-vanishing values of \(d_5\) and \(d_6\) as observed in distinction from the case of oriented nickel. We might attribute this effect to a different reaction-scheme other than (2) as suggested by the simultaneous formation of methane observed by Anderson and Kembalip and assume that \(d_5\) and \(d_6\) vanish so far as the reaction-scheme (2) as in the case of oriented nickel. If then, the values of above parameters are “normal” and the slowest step becomes I.

This conclusion is in conformity with the conclusion of the structure theory referred to the introduction that the rate of catalytic hydrogenation is governed by I or III respectively below or above the optimum temperature, the slowest step at higher temperature being III as shown in the Table.

3. In accordance with the inference of the foregoing paragraph, the catalysts are divided into two groups that of the slowest step of I or III.

4. Eq. (5) leads to
\[
2\Omega = \frac{\bar{Y}_V^{PD}}{\bar{Y}_V^P}, \quad (18)
\]

for the initial stage of the reaction with due regard to the condition of the steady state. The \(\Omega\) is however one of three parameters in the theoretical equations of distribution, which could be directly determined from the initial rates of formation of PD and \(P_3\) in gas. Observation of this sort will provide a crucial test of the present theory.
Fine Structure of Reaction Between Ethane and Deuterium

The total analysis of this subject will be published before long in this journal.

Calculations for Rh and Co, which belong to the group with the slowest step of III, are excluded here because of total percentages of deuteroethanes observed being short or excess of 100%.

Summary

1. The relative abundances of deuteroethanes observed by Anderson and Kemball are satisfactorily explained by an extension of the structure theory of the catalytic hydrogenation of ethylene, assuming further dissociation of adsorbed ethylene.
2. The conclusion that the slowest step on nickel is the one of hydrogen-chemisorption (I) or ethane-desorption (III) at lower or higher temperature agrees with that of the structure theory.
3. The metallic catalysts observed are divided into two, i.e. the one of the slowest step of I and the other of III.

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