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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

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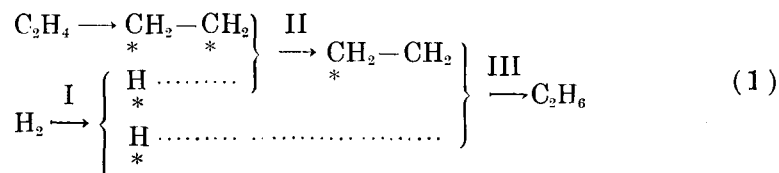
Introduction

ANDERSON and KEMBALL¹⁾ 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 deuterioethanes 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 HORIUTI²⁾, developed with special reference to the hydrogenation of ethylene in extension of the mechanism of HORIUTI and POLANYI³⁾, by the similar method to that the 'fine structure theory' of KEN⁴⁾, who analysed the catalytic deuteration of ethylene⁵⁾ and propylene⁶⁾.

Reaction Mechanism and Fine Structure Calculation

The hydrogenation and simultaneous hydrogen-exchange proceed by the scheme

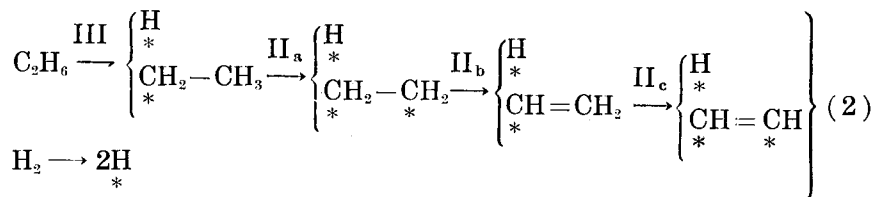


according to the structure theory, the rate of hydrogenation being controlled by I or III respectively below or above the optimum temperature, where * denotes a chemisorption site and H stands for protium

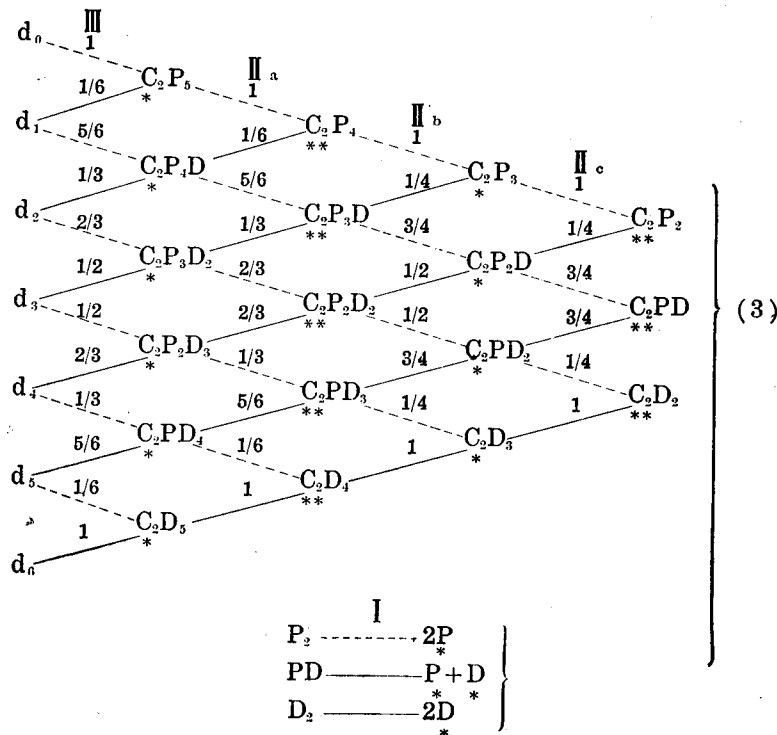
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(P) or deuterium (D).

The scheme (1) might be supplemented as



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 C_2H_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



Fine Structure of Reaction Between Ethane and Deuterium

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_0} etc. of respective deuterio-compound d_0 etc. can be expressed as

$$\left. \begin{aligned} \dot{Y}^{P_2} &= v(I) [(y^P)^2 - y^{P_2}] \\ \dot{Y}^{PD} &= v(I) [2y^P y^D - y^{PD}] \\ \dot{Y}^{D_2} &= v(I) [(y^D)^2 - y^{D_2}] \end{aligned} \right\} \quad (4)$$

for hydrogen in gas,

$$\left. \begin{aligned} \dot{Y}^{d_0} &= v(III) (y^{C_2P_2} y^P - y^{d_0}) \\ \dot{Y}^{d_1} &= v(III) (y^{C_2P_2} y^D + y^{C_2P_2D} y^P - y^{d_1}) \\ \dots\dots\dots \\ \dot{Y}^{d_6} &= v(III) (y^{C_2D_2} y^D - y^{d_6}) \end{aligned} \right\} \quad (5)$$

for ethanes in gas,

$$\left. \begin{aligned} \dot{Y}^{C_2P_2} &= v(II_a) (y^{C_2P_2} y^P - y^{C_2P_2}) + v(III) \left(y^{d_0} + \frac{1}{6} y^{d_1} - y^{C_2P_2} \right) \\ \dot{Y}^{C_2P_2D} &= v(II_a) (y^{C_2P_2} y^D + y^{C_2P_2D} y^P - y^{C_2P_2D}) + v(III) \left(\frac{5}{6} y^{d_1} + \frac{1}{3} y^{d_2} - y^{C_2P_2D} \right) \\ \dots\dots\dots \\ \dot{Y}^{C_2D_2} &= v(II_a) (y^{C_2D_2} y^D - y^{C_2D_2}) + v(III) \left(\frac{1}{6} y^{d_5} + y^{d_6} - y^{C_2D_2} \right) \end{aligned} \right\} \quad (6)$$

for adsorbed ethyl radicals,

$$\left. \begin{aligned} \dot{Y}^{C_2P_2} &= v(II_a) \left(y^{C_2P_2} + \frac{1}{6} y^{C_2P_2D} - y^{C_2P_2} \right) + v(II_b) (y^{C_2P_2} y^P - y^{C_2P_2}) \\ \dot{Y}^{C_2P_2D} &= v(II_a) \left(\frac{5}{6} y^{C_2P_2D} + \frac{1}{3} y^{C_2P_2D_2} - y^{C_2P_2D} \right) + v(II_b) (y^{C_2P_2} y^D + y^{C_2P_2D} y^P - y^{C_2P_2D}) \\ \dots\dots\dots \\ \dot{Y}^{C_2D_2} &= v(II_a) \left(\frac{1}{6} y^{C_2PD_2} + y^{C_2D_2} - y^{C_2D_2} \right) + v(II_b) (y^{C_2D_2} y^D - y^{C_2D_2}) \end{aligned} \right\} \quad (7)$$

for adsorbed ethylenes,

$$\left. \begin{aligned} \dot{Y}^{C_2P_2} &= v(II_b) \left(y^{C_2P_2} + \frac{1}{4} y^{C_2P_2D} - y^{C_2P_2} \right) + v(II_c) (y^{C_2P_2} y^P - y^{C_2P_2}) \\ \dot{Y}^{C_2P_2D} &= v(II_b) \left(\frac{3}{4} y^{C_2P_2D} + \frac{1}{2} y^{C_2P_2D_2} - y^{C_2P_2D} \right) + v(II_c) (y^{C_2P_2} y^D + y^{C_2PD_2} y^P - y^{C_2P_2D}) \\ \dot{Y}^{C_2PD_2} &= \dots\dots\dots \\ \dot{Y}^{C_2D_2} &= v(II_b) \left(\frac{1}{4} y^{C_2PD_2} + y^{C_2D_2} - y^{C_2D_2} \right) + v(II_c) (y^{C_2D_2} y^D - y^{C_2D_2}) \end{aligned} \right\} \quad (8)$$

for C_2H_3 's and

$$\left. \begin{aligned} \dot{Y}^{C_2P_2} &= v(II_c) \left(y^{C_2P_2} + \frac{1}{4} y^{C_2P_2D} - y^{C_2P_2} \right) \\ \dot{Y}^{C_2PD} &= \dots\dots\dots \\ \dot{Y}^{C_2D_2} &= \dots\dots\dots \end{aligned} \right\} \quad (9)$$

for acetylenic complexes respectively.

In above equations, y^i is the fraction of the number of i -th deuterated product (δ_i) over the total number of the product regardless of isotopes (δ), $v(j)$ 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. CP_2 - CPD_2 , CPD - CP_2D and CD_2 - CP_3 for CP_3D_2 .

Imposing on these equations the initial condition of the reaction as $y^{D_2} = y^{D_1} = 1$ and $y^{PD} = y^{P_2} = y^{D_1} = y^{D_2} = \dots = y^{D_6} = 0$, and the steady state condition with respect to every intermediate, we have

$$\left. \begin{aligned} \dot{Y}^{D_0} &= v(III) (y^{C_2P_3} y^P - 1) \\ \dot{Y}^{D_l} &= v(III) (y^{C_2P_3-lD_l} y^D + y^{C_2P_3-lD_l} y^P) \end{aligned} \right\} \quad (10)$$

(l : an integer of $1 \leq l \leq 6$) ,

$$\left. \begin{aligned} a_0 y^{C_2P_3} &= c_0 y^{C_2P_3D} + e_0 \\ a_m y^{C_2P_3-mD_m} &= b_m y^{C_2P_3-mD_{m-1}} + c_m y^{C_2P_3-mD_m} + e_m \end{aligned} \right\} \quad (11)$$

(m : an integer of $1 \leq m \leq 5$)

and

$$\left. \begin{aligned} (1 + r y^D) y^{C_2P_3} &= y^{C_2P_3} + \frac{1}{4} y^{C_2P_3D} + \frac{r}{4} y^P y^{C_2P_3D} \\ \left(1 + \frac{r}{4} + \frac{r}{2} y^D \right) y^{C_2P_2D} &= \frac{3}{4} y^{C_2P_3D} + \frac{1}{2} y^{C_2P_2D_2} + r \left(y^D y^{C_2P_3} + \frac{3}{4} y^P y^{C_2PD_2} \right) \\ \left(1 + \frac{3r}{4} y^P \right) y^{C_2PD_2} &= \frac{1}{2} y^{C_2P_2D_2} + \frac{3}{4} y^{C_2PD_3} + r \left(\frac{3}{4} y^D y^{C_2P_3D} + y^D y^{C_2D_3} \right) \\ (1 + r y^P) y^{C_2D_3} &= \frac{1}{4} y^{C_2PD_3} + y^{C_2D_3} + r y^D y^{C_2PD_2} \end{aligned} \right\} \quad (12)$$

where

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$$\left. \begin{aligned} a_0 &= \beta + y^D \\ a_1 &= \frac{1+\beta}{\alpha} - \frac{5}{6} + \frac{2}{3} y^D \\ a_2 &= \frac{1+\beta}{\alpha} - \frac{2}{3} + \frac{1}{3} y^D \\ a_3 &= \frac{1+\beta}{\alpha} - \frac{1}{3} - \frac{1}{3} y^D \\ a_4 &= \frac{1+\beta}{\alpha} - \frac{1}{6} - \frac{2}{3} y^D \\ a_5 &= \frac{1+\beta}{\alpha} - y^D \end{aligned} \right\}, \quad \left. \begin{aligned} b_1 &= y^D \\ b_2 &= \frac{5}{6} y^D \\ b_3 &= \frac{2}{3} y^D \\ b_4 &= \frac{1}{3} y^D \\ b_5 &= \frac{1}{6} y^D \end{aligned} \right\}, \quad \left. \begin{aligned} c_0 &= \frac{1}{6} y^P \\ c_1 &= \frac{1}{3} y^P \\ c_2 &= \frac{2}{3} y^P \\ c_3 &= \frac{5}{6} y^P \\ c_4 &= y^P = 1 - y^D \end{aligned} \right\},$$

$$\left. \begin{aligned} e_0 &= \frac{(1-\alpha)(1+\beta)}{\alpha} + \beta(y^P)^2 y^{C_2P_3} \\ e_1 &= \beta[2y^P y^D y^{C_2P_3} + (y^P)^2 y^{C_2P_2D}] \\ e_2 &= \beta[(y^D)^2 y^{C_2P_3} + 2y^P y^D y^{C_2P_2D} + (y^P)^2 y^{C_2PD_2}] \\ e_3 &= \dots\dots\dots \\ e_4 &= \dots\dots\dots \\ e_5 &= \beta(y^D)^2 y^{C_2D_3} \end{aligned} \right\},$$

$$\alpha = \frac{v(\text{II}_a)}{v(\text{II}_a) + v(\text{III})}, \quad \beta = \frac{v(\text{II}_b)}{v(\text{II}_a)} \quad \text{and} \quad \gamma = \frac{v(\text{II}_c)}{v(\text{II}_b)}. \quad (13)$$

The initial rates of formation of respective ethane could be, in principle, calculated by eliminating $y^{C_2P_3}$, etc., $y^{C_2P_2}$, etc. and $y^{C_2P_2}$, etc. from Eqs. (10), (11) and (12). The laborious calculation might be avoided by assuming that step II_c is isotopically equilibrium. The $y^{C_2P_3}$, etc. are then respectively expressed as $y^{C_2P_3-nD_n} \propto (y^P)^{3-n}(1-y^P)^n$ (n : an integer of $0 \leq n \leq 3$ and $\sum_{n=0}^3 y^{C_2P_3-nD_n} = 1$).

Eq. (11) is now solved as

$$\left. \begin{aligned} y^{C_2P_5} &= A_5 B_0 \\ y^{C_2P_5-mD_m} &= A_m y^{C_2P_5-mD_{m-1}} + B_m \end{aligned} \right\} \quad (14) \quad (1 \leq m \leq 5)$$

where

$$A_5 = \frac{b_5}{\alpha_5}, \quad A_{5-m} = \frac{b_{5-m}}{\alpha_{5-m} - c_{5-m} A_{6-m}}$$

$$B_5 = \frac{e_5}{a_5} \quad \text{and} \quad B_{5-m} = \frac{e_{5-m} + c_{5-m} B_{6-m}}{a_{5-m}}$$

It follows from (10) and (14)

$$\left. \begin{aligned} \dot{Y}^{d_0} &= y^p v(\text{III}) \left(y^{c_2 P_5} - \frac{1}{y^P} \right) \\ \dot{Y}^{d_m} &= y^p v(\text{III}) [y^{c_2 P_5 - m D_{m-1}} (\Omega + A_m) + B_m] \\ \dot{Y}^{d_5} &= y^p v(\text{III}) y^{c_2 D_5} \Omega \quad (1 \leq m \leq 5) \end{aligned} \right\} \quad (15)$$

where

$$\Omega = y^D / y^P .$$

The ratio of \dot{Y}^{d_1} , \dot{Y}^{d_2} , ... and \dot{Y}^{d_5} 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 α , β and y^D (or Ω). 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 associative mechanism or ANDERSON and KEMBALL'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

$$\begin{aligned} y^P [2v(\text{I}) + v(\text{II}_a) + v(\text{II}_b) + v(\text{III})] &= v(\text{II}_a) \left(y^{c_2 P_5} + \dots + \frac{1}{6} y^{c_2 P_4 D} \right) \\ &+ v(\text{II}_b) \left(y^{c_2 P_4} + \dots + \frac{1}{4} y^{c_2 P D_3} \right) + v(\text{III}) \end{aligned}$$

for P and

$$\begin{aligned} y^D [2v(\text{I}) + v(\text{II}_a) + v(\text{II}_b) + v(\text{III})] &= 2v(\text{I}) + v(\text{II}_a) \left(\frac{1}{6} y^{c_2 P_4 D} + \dots + y^{c_2 P_5} \right) \\ &+ v(\text{II}_b) \left(\frac{1}{4} y^{c_2 P_3 D} + \dots + y^{c_2 D_4} \right) \end{aligned}$$

for D respectively. From these two conditions and Eq. (16) we have

Observed and Theoretical Distributions of Deuteroethanes

| Catalyst | Reaction Temp. °C | Deuteroethane % | | | | | | | y^D | α | β | $\frac{1-\alpha}{\alpha}$ | δ | Slowest Step. |
|-------------|-------------------|-----------------|---------|---------|---------|---------|---------|---------|-------|----------|---------|---------------------------|----------|--------------------------------------|
| | | obs. calc. | d_1 | d_2 | d_3 | d_4 | d_5 | d_6 | | | | | | |
| W | -80~-29 | obs. calc. | 78 78 | 12 12.2 | 5.1 4.7 | 2.0 3.8 | 9.0 1.0 | 0.6 0.0 | 0.30 | 0.5 | 1.0 | 1.0 | 0.45 | I |
| Mo | -50~0 | obs. | 81 | 14 | 3 | 0.7 | 0 | 0 | | | | | | |
| Ta | -50~0 | obs. calc. | 81 83.1 | 15 12.5 | 3.1 2.9 | 0.6 1.4 | 0 0.2 | 0 0 | 0.20 | 0.5 | 1.0 | 1.0 | 0.09 | I |
| Ni (orient) | 0~75 | obs. calc. | 90 90.6 | 10 8.6 | 0 0.8 | 0 0 | 0 0 | 0 0 | 0.05 | 0.6 | 0.6 | 0.67 | 0.23 | I |
| Ni | 0~75 | obs. calc. | 88 88 | 8.5 8.5 | 0 0.7 | 0 0 | 0.6 0.1 | 3.0 2.4 | 0.99 | 0.2 | 1.0 | 4.0 | 269. | II _a (= II _b) |
| | 162~195 | obs. calc. | 40 43 | 10 13 | 4 3.8 | 5 2.3 | 10 10.1 | 30 27.4 | 0.92 | 0.65 | 1.0 | 0.54 | 8.0 | III |
| Zr | 158~192 | obs. calc. | 52 54.4 | 17 17.1 | 5.1 4.9 | 4.3 2.3 | 7.0 5.6 | 14 15.7 | 0.90 | 0.55 | 0.7 | 0.82 | 8.1 | III (\cong II _b) |
| Cr | 149~215 | obs. | 47 | 18 | 6.6 | 6.0 | 7.2 | 15 | | | | | | |
| V | 102~160 | obs. calc. | 46 46.9 | 19 19.4 | 5.7 7.2 | 5.1 2.8 | 7.5 5.0 | 16 18.8 | 0.95 | 0.6 | 0.5 | 0.67 | 15.7 | III (\cong II _b) |
| Pt | 184~192 | obs. calc. | 19 19.4 | 17 16.5 | 12 14.2 | 10 14.3 | 5 15.0 | 25 20.5 | 0.90 | 0.83 | 0.1 | 0.205 | 3.1 | III (\cong II _b) |
| Pd | 145~207 | obs. calc. | 5 4.2 | 6 4.5 | 8 5.2 | 11 9.3 | 19 21.7 | 52 54.7 | 0.95 | 0.99 | 0.1 | 0.01 | 1.4 | III |

Fine Structure of Reaction Between Ethane and Deuterium

$$\frac{v(\text{I})}{v(\text{IIa})} = \frac{1}{2} \left[\left(\frac{1-\alpha}{\alpha} + D' \right) \Omega - D \right] = \delta \quad (17)$$

where

$$D = \sum_{m=1}^5 f_m y^{C_2P_5-mD_m} + f_6 (1 - y^P y^{C_2P_3}),$$

$$D' = \sum_{m=1}^5 f_m y^{C_2P_m D_5-m} + f_6 (1 - y^D y^{C_2P_3}),$$

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

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

The relative rates of four steps are given by Eqs. (13) and (17) as

$$v(\text{I}) : v(\text{IIa}) : v(\text{IIb}) : v(\text{III}) = \delta : 1 : \beta : \frac{1-\alpha}{\alpha}.$$

It is seen from Table that the values of parameters α and δ 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 KEMBALL,¹⁾ 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

$$2\Omega = \dot{Y}^{PD} / \dot{Y}^{P_2} \quad (18)$$

for the initial stage of the reaction with due regard to the condition of the steady state. The Ω 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_2 in gas. Observation of this sort will provide a crucial test of the present theory.

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 deuterioethanes observed being short or excess of 100%.

Summary

1. The relative abundances of deuterioethanes 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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