



Title	FINE STRUCTURE OF REACTION BETWEEN ETHANE AND DEUTERIUM ON VARIOUS EVAPORATED METAL FILMS : Explanation to ANDERSON and KEMBALL's Experiment
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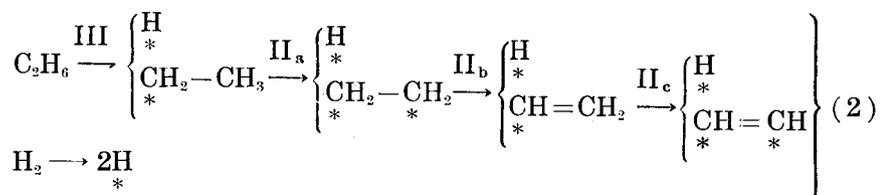


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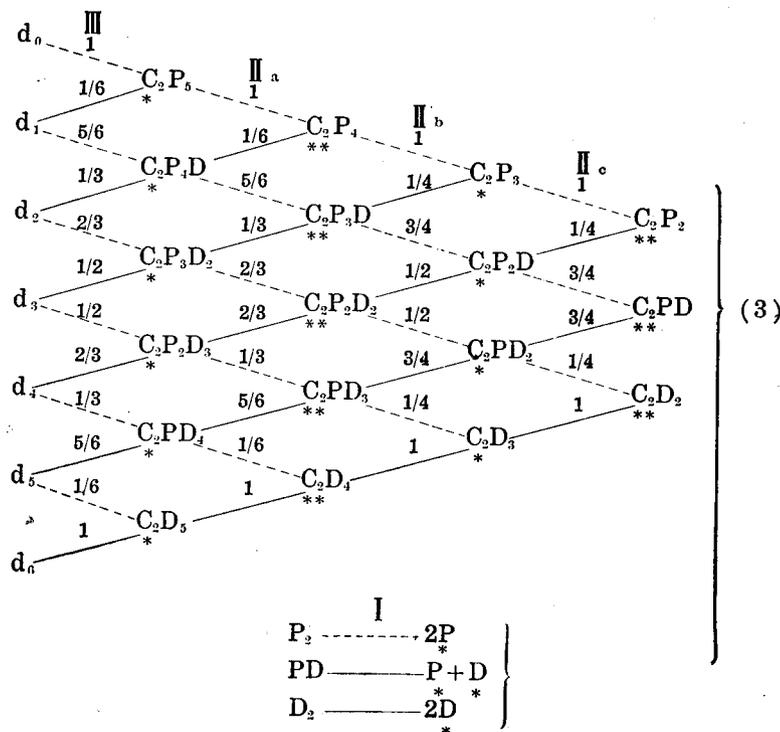


(P) or deuterium (D).

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<sup>(7),(9)</sup>. The intermediate  $\text{C}_2\text{H}_3$  has been proposed by FARKAS<sup>(8)</sup> with reference to his dissociative mechanism, whereas  $\text{CH}=\text{CH}$  or the 'acetylenic complex' by BECK<sup>(9)</sup> 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

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

for hydrogen in gas,

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

for ethanes in gas,

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

for adsorbed ethyl radicals,

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

for adsorbed ethylenes,

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

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,  $y^{\delta_i}$  is the fraction of the number of  $i$ -th deuterated product ( $\delta_i$ ) 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.  $CP_2$ - $CPD_2$ ,  $CPD$ - $CP_2D$  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

Fine Structure of Reaction Between Ethane and Deuterium

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

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

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

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<sub>c</sub> 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)

$$\left. \begin{aligned} \dot{Y}^{d_0} &= y^P v(\text{III}) \left( y^{C_2P_5} - \frac{1}{y^P} \right) \\ \dot{Y}^{d_m} &= y^P v(\text{III}) [y^{C_2P_5 - mD_{m-1}} (\Omega + A_m) + B_m] \\ \dot{Y}^{d_5} &= y^P v(\text{III}) y^{C_2D_5} \Omega \quad (1 \leq m \leq 5) \end{aligned} \right\} \quad (15)$$

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  $\alpha$ ,  $\beta$  and  $y^D$  (or  $\Omega$ ). 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

$$\begin{aligned} y^P [2v(\text{I}) + v(\text{II}_a) + v(\text{II}_b) + v(\text{III})] &= v(\text{II}_a) \left( y^{C_2P_5} + \dots + \frac{1}{6} y^{C_2P_4D} \right) \\ &+ v(\text{II}_b) \left( y^{C_2P_4} + \dots + \frac{1}{4} y^{C_2PD_3} \right) + v(\text{III}) \end{aligned}$$

for P and

$$\begin{aligned} y^D [2v(\text{I}) + v(\text{II}_a) + v(\text{II}_b) + v(\text{III})] &= 2v(\text{I}) + v(\text{II}_a) \left( \frac{1}{6} y^{C_2P_4D} + \dots + y^{C_2P_5} \right) \\ &+ v(\text{II}_b) \left( \frac{1}{4} y^{C_2P_3D} + \dots + y^{C_2D_4} \right) \end{aligned}$$

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

Observed and Theoretical Distributions of Deuteroethanes

Catalyst	Reaction Temp. °C	Deuteroethane %							$y^D$	$\alpha$	$\beta$	$\frac{1-\alpha}{\alpha}$	$\delta$	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 <sub>a</sub> (= II <sub>b</sub> )
	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 <sub>b</sub> )
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 <sub>b</sub> )
Pt	134~192	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 <sub>b</sub> )
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

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

$$D' = \sum_{m=1}^5 f_m y^{C_2P} m^{D_m} + f_6 (1 - y^D y^{C_2P_3}),$$

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

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

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  $\alpha$  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 KEMBALL,<sup>1)</sup> 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  $\Omega$  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  $P_2$  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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