



Title	EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 4(3), 177-184
Issue Date	1957-03
Doc URL	http://hdl.handle.net/2115/24646
Type	bulletin (article)
File Information	4(3)_P177-184.pdf



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EXCHANGE REACTION BETWEEN METHANE AND DEUTERIUM

By

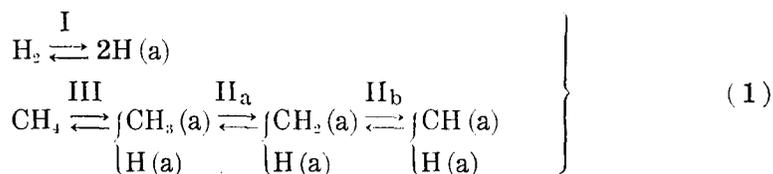
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(Received November 19, 1956)

§ 1. Introduction

KEMBALL^{1) 2)} has observed the rates of formation of different deuteromethanes from methane and deuterium on nickel and other metallic films and found that the initial rates of formation are of such relative magnitudes as $\text{CH}_3\text{D} > \text{CH}_2\text{D}_2 < \text{CHD}_3 < \text{CD}_4$ for all metals. He has also found that the activation energy of the initial formation of CH_3D , e. g. on nickel, is 24 kcal, whereas those of CH_2D_2 , CHD_3 and CD_4 on the same metal are commonly 31 kcal/mole.¹⁾ He concluded from these results that two kinds of reactions are going on, each forming CH_3D or the latter group of deuteromethanes.

In the present paper above experimental results are systematically deduced from the dissociative scheme,

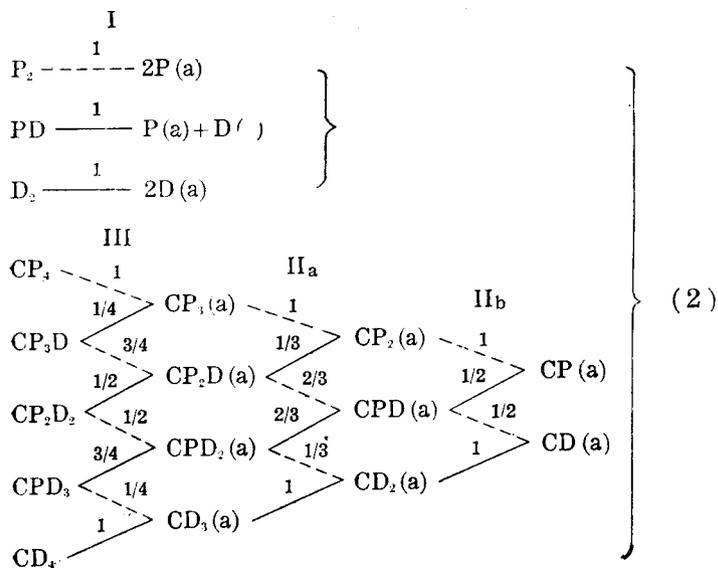


where H stands for protium P and deuterium D, and a few conclusions accessible to the experimental test inferred from the result of the analysis.

§ 2. Detailed Scheme and Qualitative Explanation

Scheme (1) may be developed discriminating between P and D as

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where the dotted or full line denotes the transfer of P or D respectively and the annexed number indicates the fraction of the rate of dissociation specified by the line, of the atom group on its left over the total rate of dissociation of the same atom group, identifying the kinetic behaviour of D with that of P.

On the basis of the Scheme (2) the KEMBALL's experimental results at the initial stage of the reaction will first be qualitatively accounted for as follows, assuming that the overall equilibrium of the respective step is established, i.e. the overall forward and backward rates of each step are balanced with each other aside from the isotopic difference and that I and II_b, among them are sufficiently quick that they are even isotopically in equilibrium.

The rate of formation of CP₃(a) through III is large compared with those of CP₂D(a), CPD₂(a) and CD₃(a), inasmuch as the concentrations of deuteromethanes are small compared with that of CP₄ at the initial stage of the reaction. Chemisorbed hydrogen atoms consist on the other hand practically exclusively of deuterium and CD₂(a) must be much abundant compared with CP₂(a) and CPD(a) on account of the isotopic equilibrium of I and II_b; the rates of formation of CPD₂(a) and

lower substitution products through II_a are in consequence now negligibly small compared with that of CD₃(a).

As the result both of the above situations CP₂D(a) and CPD₂(a) must be less abundant compared with CP₃(a) or CD₃(a). The rate of formation of CP₃D, CP₂D₂, CPD₃ or CD₄ is now given practically by that of combination of D(a) and CP₃(a) *etc.* respectively and hence the rates of formation of CP₃D and CD₄ must be large compared with those of CP₂D₂ and CPD₃ at the initial stage of the exchange reaction as observed by KEMBALL. This qualitative explanation is now followed by detailed calculation adjusting the relative rates of each steps, assuming the isotopic equilibrium of II_b only but not that of I.

§ 3. Calculation of the Fine Structure

The rate of formation of every atom group in the Scheme (2) is given as

$$\left. \begin{aligned} V^{P_2} &= V(\text{I})\{(y^P)^2 - y^{P_2}\} \\ V^{PD} &= V(\text{I})\{2y^P y^D - y^{PD}\} \\ V^{D_2} &= V(\text{I})\{(y^D)^2 - y^{D_2}\} \end{aligned} \right\} \quad (3. a)$$

$$\left. \begin{aligned} V^{CP_3} &= V(\text{III}) (y^{CP_3} y^P - y^{CP_3}) \\ V^{CP_2D} &= V(\text{III}) (y^{CP_2} y^D + y^{CP_2D} y^P - y^{CP_2D}) \\ V^{CP_2D_2} &= V(\text{III}) (y^{CP_2D} y^D + y^{CP_2D_2} y^P - y^{CP_2D_2}) \\ V^{CPD_2} &= V(\text{III}) (y^{CPD_2} y^D + y^{CPD_2} y^P - y^{CPD_2}) \\ V^{CD_4} &= V(\text{III}) (y^{CD_3} y^D - y^{CD_4}) \end{aligned} \right\} \quad (3. b)$$

$$\left. \begin{aligned} V^{CP_3} &= V(\text{III}) \left(y^{CP_3} + \frac{1}{4} y^{CP_2D} - y^{CP_3} \right) + V(\text{II}_a) (y^{CP_2} y^P - y^{CP_3}) \\ V^{CP_2D} &= V(\text{III}) \left(\frac{3}{4} y^{CP_2D} + \frac{1}{2} y^{CP_2D_2} - y^{CP_2D} \right) + V(\text{II}_a) (y^{CP_2} y^D + y^{CP_2D} y^P - y^{CP_2D}) \\ V^{CP_2D_2} &= V(\text{III}) \left(\frac{1}{2} y^{CP_2D_2} + \frac{3}{4} y^{CP_2D_2} - y^{CP_2D_2} \right) + V(\text{II}_a) (y^{CP_2D} y^D + y^{CP_2D_2} y^P - y^{CP_2D_2}) \\ V^{CPD_2} &= V(\text{III}) \left(\frac{1}{4} y^{CPD_2} + y^{CPD_2} - y^{CPD_2} \right) + V(\text{II}_a) (y^{CPD_2} y^D - y^{CPD_2}) \end{aligned} \right\} \quad (3. c)$$

and so on for V^{CP_2} etc., V^{CP} and V^{CD} respectively, where $V(j)$ ($j=I, \text{II}_a$ or III) denotes the overall forward or backward rate of the step j at overall equilibrium, and y^P the fraction of the number of P(a) over the sum of the numbers of P(a) and D(a), y^{CP_3} the fraction of the

number of CP_4 over the sum of those of CP_4 , CP_3D , CP_2D_2 , CPD_3 and CD_4 , and so on.

The y^{CP_2} , y^{CPD} or y^{CD_2} may be expressed, because of the isotopic equilibrium of II_b , as

$$y^{CP_2} = (y^P)^2, \quad y^{CPD} = 2y^P y^D, \quad y^{CD_2} = (y^D)^2. \quad (4)$$

Specializing Eqs. (3.b) and (3.c) to the initial condition, i.e. $y^{D_2} = y^{CP_4} = 1$ and $y^{PD} = y^{P_2} = y^{CP_3D} = \dots = y^{CD_4} = 0$, and putting rates V^{CP_3} , etc. of intermediates $CP_3(a)$ etc. individually zero for the steady state, we have

$$V^{CP_4} = V(III) (1-y^D) \left\{ (1-\alpha) + \alpha(1-y^D)^3 - \frac{1}{1-y^D} \right\} \quad (5.0)$$

$$V^{CP_3D} = V(III) \alpha y^D \left\{ \frac{1-\alpha}{\alpha} + 4(1-y^D)^3 \right\} \quad (5.1)$$

$$V^{CP_2D_2} = 6V(III) \alpha (y^D)^2 (1-y^D)^2 \quad (5.2)$$

$$V^{CPD_3} = 4V(III) \alpha (y^D)^3 (1-y^D) \quad (5.3)$$

$$V^{CD_4} = V(III) \alpha (y^D)^4 \quad (5.4)$$

where

$$\alpha = \frac{V(II_a)}{V(II_a) + V(III)} \quad (5.a)$$

The values of α and y^D are adjusted according to the above equations to the experimental results of KEMBALL at 6.4 mmHg partial pressures both of D_2 and CP_4 . V^{CP_3D} etc. calculated from these values of α and y^D are in good agreement with observed values as shown in Table I.

The third last column of the Table shows the relative rate $V(III)/V(II_a)$ calculated from α determined as above according to (5.a). The next column gives $V(I)/V(II_a)$ calculated by equation

$$V(I)/V(II_a) = y^D (1-\alpha^2)/2\alpha (1-y^D) \quad (6)$$

which follows from (5.a), (4), the steady state equation for D(a) at the initial stage, i.e.

$$y^D \left\{ 2V(I) + V(II_a) + V(III) \right\} = V(II_a) \left(\frac{1}{3} y^{CP_3D} + \frac{2}{3} y^{CPD_2} + y^{CD_3} \right) + 2V(I),$$

those for $CP_2D(a)$, $CPD_2(a)$ and $CD_3(a)$ obtained from last three equations of (3.c)*) putting the left side of each equal to zero and the relation, $y^P + y^D = 1$, by eliminating from these nine equations eight quantities

*) The equation obtained similarly from the first of (3.c) is not linearly independent from these equations.

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i. e. y^{CP_2D} , y^{CPD_2} , y^{CD_3} , y^{CP_2} , y^{CPD} , y^{CD_2} , y^P and $V(III)/V(II_a)$.

§ 4. Discussion

1). It has been assumed in the qualitative explanation that the step I is practically in isotopic equilibrium and hence y^D is nearly unity, whereas in the numerical calculation y^D was not assumed unity but adjusted to the experiments. The result shown in Table I confirms this assumption in the qualitative explanation. The second term in the parenthesis of (5.1) is now negligible in accordance with this result.

TABLE I. Observed and calculated relative rates of the initial formation of deuteromethanes at partial pressures $P_{D_2} = P_{CP_4} = 6.4$ mmHg.

Catalyst	Reaction temp. °C	Relative formation-rate of deuteromethane (%)				α	y^D	$\frac{V(III)}{V(II_a)}$	$\frac{V(I)}{V(II_a)}$	Slowest step	
		Remark	CP ₃ D	CP ₂ D ₂	CPD ₃						CD ₄
Ni *)	228	obs.	13.2	2.2	20.3	64.4	0.865	0.925	0.156	1.800	III
		calc.	13.0	2.6	19.5	64.9					
	255	obs.	10.2	2.3	20.4	67.6	0.900	0.925	0.111	1.302	III
		calc.	9.6	2.6	20.4	66.4					
Rh	162	obs.	17	4	22	57	0.800	0.900	0.250	1.80	III
		calc.	18.6	3.8	23.8	53.6					
Pt	259.3	obs.	44	15	17	24	0.500	0.850	1.000	4.25	II _a = III
		calc.	45.6	5.4	19.9	28.1					
W	150.6	obs.	72	3	11	14	0.260	0.830	2.770	8.75	II _a
		calc.	70.8	3.6	11.5	14.1					
Pd	254.3	obs.	94.6	1.3	2.0	2.0	0.040	0.800	24.00	49.92	II _a
		calc.	95.2	0.8	2.0	2.0					
Ni *)	341	obs.	5	5	20	70	0.956	0.925	0.046	0.555	III
		calc.	3.9	2.8	22.9	70.4					

*) Reactions on this metal are of $P_{D_2} = 4.85$ and $P_{CP_4} = 6.48$ mmHg.

2. It has been observed by KEMBALL that the activation energy of the formation of CP₂D₂, CPD₃ or CD₄ on nickel is practically of a common value as mentioned above. It is concluded from this result in accordance with Eqs. (5.1), ... (5.4) that y^D is a constant practically

independent of temperature over its observed range; this conclusion is in accordance with the results of analysis at 228°C and 255°C for nickel as shown in Table I.

3. On the basis of the temperature independence of y^D concluded above the relative rates of formation of different deuteromethanes at 341°C are now calculated as below and compared with the experimental results of KEMBALL.

The activation energies of the formation of CP_3D and CP_2D_2 are expressed from Eqs. (5.1), (5.2) and (5.a) taking y^D constant as

$$E^{CP_3D} = 2E(III) - E(II_a + III)$$

$$E^{CP_2D_2} = E(III) + E(II_a) - E(II_a + III),$$

where $E(II_a)$, $E(III)$ or $E(II_a + III)$ denotes the appropriate activation energy, e. g. $RT^2 \frac{d \ln V(II_a)}{dT}$, of $V(II_a)$, $V(III)$ or $V(II_a) + V(III)$ respectively. We have from the above relations and the observed values, $E^{CP_3D} = 24$ kcal and $E^{CP_2D_2} = 31$ kcal mentioned in the introduction,

$$E(II_a) - E(III) = 7 \text{ kcal.} \quad (7)$$

on nickel, while the same quantity is given as 6.7 kcal from values of $V(III)/V(II_a)$ at 228°C and 255°C on nickel in Table I in very satisfactory agreement.

The values of $V(III)/V(II_a)$ on nickel at 341°C is now determined from that at 228°C and (7) at 0.0427, from which we have $\alpha_{III} = 0.956$ according to (5.a). The V^{CP_3D} etc. at 341°C on nickel are now calculated according to Eqs. (5.1), ... (5.4) for the same value of y^D as that at 228°C, i. e. 0.925, and compared with those observed by KEMBALL in the last row of the Table I. The $V(I)/V(II_a)$ in the Table is similarly calculated according to Eq. (6). The calculation accounts for the experimental result that the initial rates of formation are of the relative magnitudes, $V^{CP_3D} \cong V^{CP_2D_2} < V^{CPD_3} < V^{CPD_4}$.

The latter experimental result may be understood with reference to the appreciable relative decay of $V(III)$ from 228°C to 341°C as seen in Table I, which upholds V^{CP_3D} as qualitatively stated in § 2, rather than by attributing to the difference of the evaporated films⁽¹⁾.

4. The individual values of $E(I)$ etc. on nickel are estimated as below on the basis of the relative magnitudes of rates of formation of deuteromethanes.

As y^D on nickel is close to unity, V^{CP} may be identified with

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— $V(\text{III})$ neglecting the first two terms in the parenthesis { } of (5.0). We have hence

$$E(\text{III}) = 30 \text{ kcal}$$

from the observed values of V^{CD} at 255°C and 214°C, i. e. — 0.3892% and — 0.0346% respectively of total methanes per min per mg of the metallic film. $E(\text{II}_a)$ is now obtained from the above value of $E(\text{III})$ and (7) as

$$E(\text{II}_a) = 37 \text{ kcal}$$

We have on the other hand from three values of $V(\text{I})/V(\text{II}_a)$ at 228°C, 255°C and 341°C given in Table I consistently

$$E(\text{II}_a) - E(\text{I}) = 6 \text{ kcal,}$$

and hence

$$E(\text{I}) = 31 \text{ kcal.}$$

This value of $E(\text{I})$ is considerably large compared with the value of the activation energy 13 kcal or 12 kcal of the chemisorption of hydrogen determined by the analysis of exchange reaction between hydrogen and water³⁾ or ammonia⁴⁾ respectively.

These values of $E(\text{I})$ etc. lead to a conclusion that the slowest step on nickel must be always $V(\text{III})$ even at sufficiently high temperature above those of KEMBALL's experiment.

5. The ratio of V^{CD} and V^{D} is given by (3. a) as

$$V^{\text{CD}}/V^{\text{D}} = 2y^{\text{D}}/(1-y^{\text{D}})$$

for the initial stage where $y^{\text{D}} = 1$ and $y^{\text{HD}} = y^{\text{H}} = 0$. Above equation shows that the direct determination of $V^{\text{CD}}/V^{\text{D}}$ will check the value of y^{D} determined at present by analysis of the observation of V^{CD} , etc. It must be that $V^{\text{CD}} > V^{\text{D}}$ for all metals in Table I according to the equation above, since y^{D} is nearly unity at the initial conditions according to the analysis.

If the step I were slowest, y^{D} should approach zero as D(a) supplied by the step is readily washed by protium from methane. In that case we have $V^{\text{CD}} < V^{\text{D}}$ on the contrary to the above and further according to Eqs. (5.0), ... (5. a)

$$V^{\text{CD}} : V^{\text{CD,D}} : V^{\text{CD,D}_2} : V^{\text{CD,D}_3} : V^{\text{CD}_4} = 1 : 4y^{\text{D}} : 6(y^{\text{D}})^2 : 4(y^{\text{D}})^3 : (y^{\text{D}})^4$$

i. e. that the rate decreases monotoneously along with increasing substitution with deuterium atoms.

Summary

1. The relative rates of formation of different deuteromethanes at the initial stage of the reaction observed by KEMBALL are satisfactorily explained by a reaction scheme consisting of the chemisorption of hydrogen and the successive dissociative chemisorption of methane molecule, and the results obtained are discussed especially for the case of nickel film.

2. The activation energy on nickel is determined as 31, 30 or 37 kcal for the step $H \rightleftharpoons 2H(a)$, $CH_4 \rightleftharpoons CH_3(a) + H(a)$ or $CH_3(a) \rightleftharpoons CH_2(a) + H(a)$ respectively.

3. It is concluded for the case of nickel that the fraction of the chemisorbed deuterium over the total chemisorbed hydrogen is a constant practically independent of temperature and that the slowest step must be always $CH_4 \rightleftharpoons CH_3(a) + H(a)$ even at sufficiently high temperature above those of KEMBALL's experiment.

4. It is predicted that the initial rate of formation of PD must be larger than that of P_2 for all metals observed by KEMBALL at his experimental conditions, but it must be the reverse in the case when the chemisorption of hydrogen is slowest.

5. The relative rates of formation of different deuteromethanes at the initial stage of the reaction are inferred for the case when the chemisorption of hydrogen is slowest.

The author wishes to express his sincere thanks to Professor J. HORIUTI for his kind interest and valuable discussions on the present work and also to the Ministry of Education for the Grant for the Scientific Researches.

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