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EXCHANGE REACTION OF DEUTEROETHYLENE ON NICKEL

By

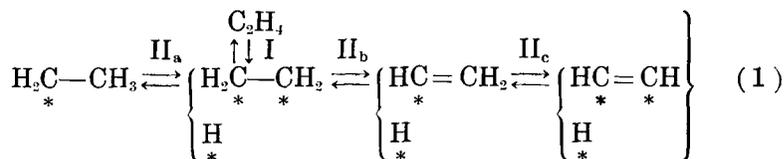
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§ 1. Introduction

FLANAGAN and RABINOVITCH¹⁾ has recently observed the rate of catalysed formation of different deuterioethylenes from trans-dideutero-ethylene or from 1:1 mixture of light and tetradeutero-ethylene in the presence of nickel wire and explained their experimental results quantitatively by a scheme involving chemisorbed hydrogen atom and ethyl radical as intermediates, taking the isotopic difference of rates into account. They assumed in their explanation that ethylene dissociates to form chemisorbed hydrogen atoms once for all initially but never later. This implies an abrupt change of the catalytic activity at the first interaction of the catalyst with ethylene, which is rather improbable.

The present paper deals with an alternative explanation without such an assumption but based on the reaction scheme



consistently related to the schemes which satisfactorily accounted for the experimental results of the catalytic exchange reaction between ethane and deuterium²⁾ or between acetylene and deuterioacetylene³⁾ and of the catalytic hydrogenation of ethylene⁴⁾, where H stands for protium P and deuterium D, and * signifies the bond of chemisorption. I, II_a, II_b and II_c are steps respectively in overall equilibrium but not

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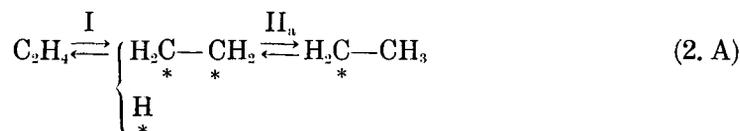
necessary in the exchange equilibrium, i.e. the isotopically detailed equilibrium.

It is concluded from the results of the analysis that the chemisorption I of ethylene, although quickest among the steps of the Scheme (1) at observed temperatures, may control the exchange reaction at sufficiently low temperatures and hence a prediction accessible to experimental test is deduced.

The present author has further investigated the statement of FLANAGAN and RABINOVITCH that their rate equations have been derived both from the Rideal mechanism and the associative mechanism. It is now shown that their rate equations are derived from the Rideal mechanism but not generally from the associative mechanism, provided that the Rideal mechanism as called by them is formulated as



and the so-called associative mechanism as

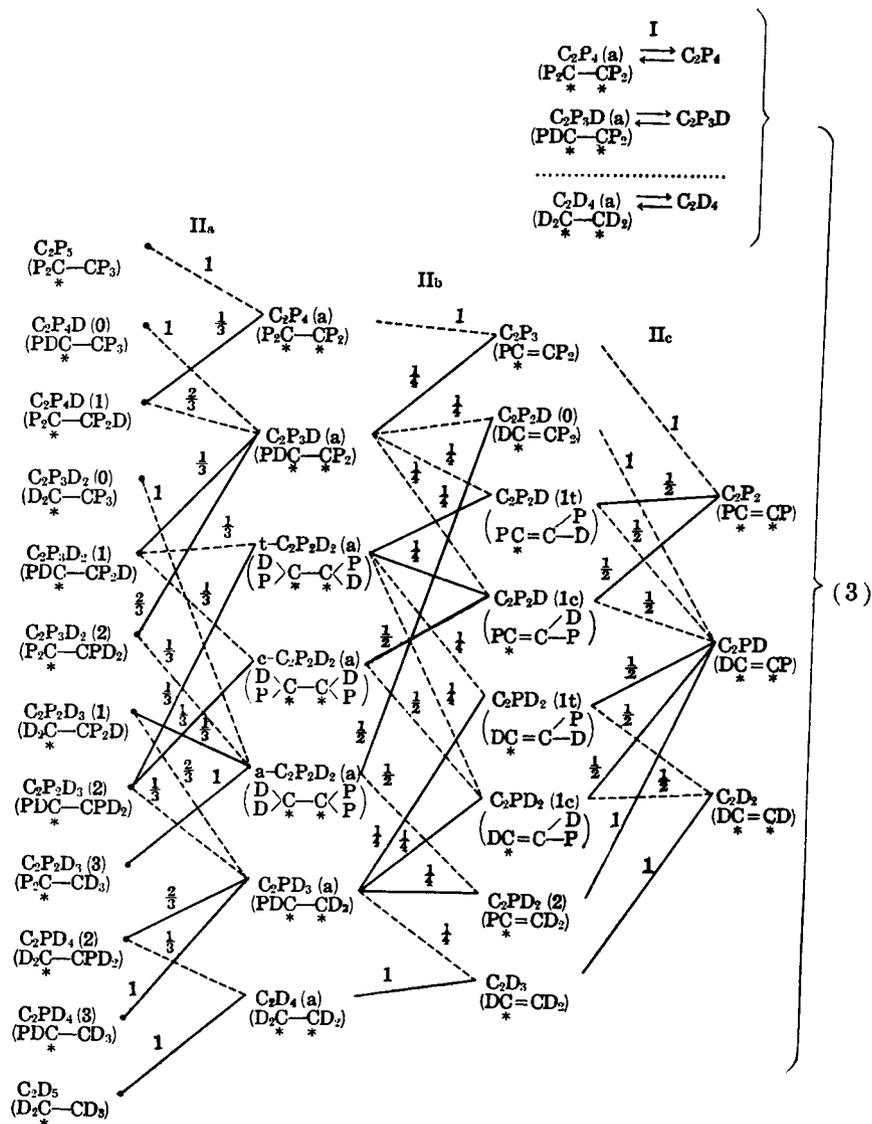


where H may be supplied either as assumed by FLANAGAN and RABINOVITCH or as in (1), i.e. by steps II_b and II_c; the so-called associative mechanism or (2. A) leads to the rate equations of FLANAGAN and RABINOVITCH in the extreme case when I is quick enough to attain the exchange equilibrium and hence (2. R) and (2. A) are kinetically identical with each other.

§ 2. The Detailed Scheme and the Rate Equations

Scheme (1) is now developed, discriminating between P and D and denoting trans-, cis- or asymmetric dideuteroethylene by t-, c- or a-C₂P₂D₂ respectively, as

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$$\begin{aligned}
 & + \frac{1}{3} y^{C_2P_2D_2(1)} + y^{C_2P_2D_2(3)} - y^{a-C_2P_2D_2(a)} \\
 & + V(II_c)(y^{C_2P_2D_2(0)}y^D + y^{C_2PD_2(2)}y^P - y^{a-C_2P_2D_2(a)}) \\
 V^{C_2PD_3(a)} = & V(I)(y^{C_2PD_3} - y^{C_2PD_3(a)}) + V(II_a) \left(\frac{2}{3} y^{C_2P_2D_2(1)} + \frac{1}{3} y^{C_2P_2D_2(2)} \right. \\
 & + \frac{2}{3} y^{C_2PD_2(2)} + y^{C_2PD_2(3)} - y^{C_2PD_3(a)} \left. \right) + V(II_b)(y^{C_2PD_2(1t)}y^D \\
 & + y^{C_2PD_2(1c)}y^D + y^{C_2PD_2(2)}y^D + y^{C_2D_3}y^P - y^{C_2PD_3(a)}) \\
 V^{C_2D_4(a)} = & V(I)(y^{C_2D_4} - y^{C_2D_4(a)}) + V(II_a) \left(\frac{1}{3} y^{C_2PD_2(2)} + y^{C_2D_3} - y^{C_2D_4(a)} \right) \\
 & + V(II_c)(y^{C_2D_3}y^D - y^{C_2D_4(a)}) ,
 \end{aligned}$$

and for chemisorbed ethyl radicals

$$\begin{aligned}
 V^{C_2P_3} &= V(II_a)(y^{C_2P_3(a)}y^P - y^{C_2P_3}) \\
 V^{C_2P_3D(0)} &= V(II_a) \left(\frac{1}{2} y^{C_2P_3D(a)}y^P - y^{C_2P_3D(0)} \right) \\
 V^{C_2P_3D(1)} &= V(II_a) \left(y^{C_2P_3(a)}y^D + \frac{1}{2} y^{C_2P_3D(a)}y^P - y^{C_2P_3D(1)} \right) \\
 V^{C_2P_3D_2(0)} &= V(II_a) \left(\frac{1}{2} y^{a-C_2P_2D_2(a)}y^P - y^{C_2P_3D_2(0)} \right) \\
 V^{C_2P_3D_2(1)} &= V(II_a) \left(\frac{1}{2} y^{C_2P_3D(a)}y^D + y^{t-C_2P_2D_2(a)}y^P + y^{c-C_2P_2D_2(a)}y^P - y^{C_2P_3D_2(1)} \right) \\
 V^{C_2P_3D_2(2)} &= V(II_a) \left(\frac{1}{2} y^{C_2P_3D(a)}y^D + \frac{1}{2} y^{a-C_2P_2D_2(a)}y^P - y^{C_2P_3D_2(2)} \right) \\
 V^{C_2P_3D_3(1)} &= V(II_a) \left(\frac{1}{2} y^{a-C_2P_2D_2(a)}y^D + \frac{1}{2} y^{C_2PD_3(a)}y^P - y^{C_2P_3D_3(1)} \right) \\
 V^{C_2P_3D_3(2)} &= V(II_a) \left(y^{t-C_2P_2D_2(a)}y^D + y^{c-C_2P_2D_2(a)}y^D + \frac{1}{2} y^{C_2PD_3(a)}y^P - y^{C_2P_3D_3(2)} \right) \\
 V^{C_2P_3D_3(3)} &= V(II_a) \left(\frac{1}{2} y^{a-C_2P_2D_2(a)}y^D - y^{C_2P_3D_3(3)} \right) \\
 V^{C_2PD_3(2)} &= V(II_a) \left(\frac{1}{2} y^{C_2PD_3(a)}y^D + y^{C_2D_4(a)}y^P - y^{C_2PD_3(2)} \right) \\
 V^{C_2PD_3(3)} &= V(II_a) \left(\frac{1}{2} y^{C_2PD_3(a)}y^D - y^{C_2PD_3(3)} \right) \\
 V^{C_2D_3} &= V(II_a)(y^{C_2D_3}y^D - y^{C_2D_3}) .
 \end{aligned} \tag{4. c}$$

The $y^{C_2P_3}$, $y^{C_2P_3D(0)}$, .. and $y^{C_2D_3}$ are expressed, in accordance with the conclusion of the previous paper^{2,3)} that the step II_c is quick enough to attain the exchange equilibrium, as

$$\left. \begin{aligned} y^{C_2P_3} &= (y^P)^3 \\ y^{C_2P_2D(0)} &= y^{C_2P_2D(1t)} = y^{C_2P_2D(1c)} = (y^P)^2 y^D \\ y^{C_2PD_2(1t)} &= y^{C_2PD_2(1c)} = y^{C_2PD_2(2)} = y^P (y^D)^2 \\ y^{C_2D_3} &= (y^D)^3 \end{aligned} \right\} \quad (5)$$

The above developments are now applied below to the analysis of experimental results.

i) The isomerization of trans-dideuteroethylene at 75°C.

Specializing Eqs. (4. b) and (4. c) to the initial conditions, i. e.,

$$y^{t-C_2P_2D_2} = 1, \quad y^{C_2P_4} = y^{c-C_2P_2D_2} = y^{a-C_2P_2D_2} = y^{C_2PD_3} = y^{C_2D_4} = 0 \quad (6)$$

for the reaction of trans-dideuteroethylene at 75°C, putting rates $V^{C_2P_4(a)}$ etc. of intermediates P_2C-CP_2 etc. individually zero for the steady state, and eliminating $y^{C_2P_3}$ etc. and $y^{C_2P_2}$ etc. from the resulting equations, we have

$$\left. \begin{aligned} \left(1 - \alpha \frac{1+2y^P}{3}\right) y^{C_2P_4(a)} &= \frac{\alpha y^P}{6} y^{C_2P_3D(a)} + \beta (y^P)^4 \\ \left(1 - \alpha \frac{3+2y^P}{6}\right) y^{C_2P_3D(a)} &= \frac{\alpha}{3} (2y^{C_2P_4(a)} y^D + y^{t-C_2P_2D_2(a)} y^P + y^{c-C_2P_2D_2(a)} y^P \\ &\quad + y^{a-C_2P_2D_2(a)} y^P) + 4\beta (y^P)^3 y^D \\ \left(1 - \frac{\alpha}{3}\right) y^{t-C_2P_2D_2(a)} &= (1 - \alpha - \beta) + \frac{\alpha}{6} (y^{C_2P_3D(a)} y^D + 2y^{c-C_2P_2D_2(a)}) \\ &\quad + y^{C_2PD_3(a)} y^P + 3\beta (y^P y^D)^2 \\ \left(1 - \frac{\alpha}{3}\right) y^{c-C_2P_2D_2(a)} &= \frac{\alpha}{6} (y^{C_2P_3D(a)} y^D + 2y^{t-C_2P_2D_2(a)} + y^{C_2PD_3(a)} y^P) + \beta (y^P y^D)^2 \\ \left(1 - \frac{2\alpha}{3}\right) y^{a-C_2P_2D_2(a)} &= \frac{\alpha}{6} (y^{C_2P_3D(a)} y^D + y^{C_2PD_3(a)} y^P) + 2\beta (y^P y^D)^2 \\ \left(1 - \alpha \frac{3+2y^D}{6}\right) y^{C_2PD_3(a)} &= \frac{\alpha}{3} (y^{t-C_2P_2D_2(a)} y^D + y^{c-C_2P_2D_2(a)} y^D + y^{a-C_2P_2D_2(a)} y^D \\ &\quad + 2y^{C_2D_4(a)} y^P) + 4\beta y^P (y^D)^3 \\ \left(1 - \alpha \frac{1+2y^D}{3}\right) y^{C_2D_4(a)} &= \frac{\alpha}{6} y^{C_2PD_3(a)} y^D + \beta (y^D)^4 \end{aligned} \right\} \quad (7. y)$$

where

$$\alpha \equiv V(II_a) / \{V(I) + V(II_a) + V(II_b)\} \quad \text{and} \quad \beta \equiv V(II_b) / \{V(I) + V(II_a) + V(II_b)\}. \quad (7. a), (7. \beta)$$

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The $y^{C_2P,(a)}$ etc. are now solved as functions of α and β from the six independent equations of (7.y), and the relations

$$y^{C_2P,(a)} + y^{C_2P_2D(a)} + \dots + y^{C_2PD_3(a)} + y^{C_2D_4(a)} = 1$$

and

$$y^P = y^D = \frac{1}{2}, \quad (8)$$

which follows from (6) by neglecting the isotopic difference in rates, as

$$y^{C_2P,(a)} = 1 + \sum_m B_m, \quad y^n = A_n y^{C_2P,(a)} - B_m \quad (9.y)$$

and

$$\left. \begin{aligned} A &= 12 \left(\frac{1}{\alpha} - \frac{2}{3} \right) \\ A_{t-2} &= A_{c-2} = A_{a-2} = \alpha (A_1 + A_3) / 12 \left(1 - \frac{2\alpha}{3} \right) \\ A_3 &= \left\{ \left(1 - \frac{2\alpha}{3} \right) A_1 - \frac{\alpha}{3} \right\} / \left(1 - \frac{2\alpha}{3} - \frac{12\alpha^2}{3-2\alpha} \right) \\ A_4 &= A_3 / A_1 \\ B_1 &= 3\beta / 16\alpha \\ B_{t-2} &= -\frac{1-\alpha-\beta}{2} \left(\frac{6-2\alpha}{3-2\alpha} \right) + \frac{1}{A_1} (B_1 + B_3) - \frac{\beta(9-2\alpha)}{16(3-2\alpha)} \\ B_{c-2} &= -\frac{1-\alpha-\beta}{2} \left(\frac{2\alpha}{3-2\alpha} \right) + \frac{1}{A_1} (B_1 + B_3) - \frac{\beta(3+2\alpha)}{16(3-2\alpha)} \\ B_{a-2} &= \frac{1}{A_1} (B_1 + B_3) - \frac{3\beta}{8(3-2\alpha)} \\ B_3 &= \left\{ -\frac{\beta(12-7\alpha)}{16(3-2\alpha)} + \left(1 - \frac{2\alpha}{3} \right) B_1 + \frac{\beta}{4} \right\} / \left(1 - \frac{2\alpha}{3} - \frac{12\alpha^2}{3-2\alpha} \right) \\ B_4 &= \frac{3}{4(3-2\alpha)} \left(\frac{B_3}{3} - \frac{\beta}{4} \right) \end{aligned} \right\} (9.A,B)$$

where $m \equiv 1, t-2, c-2, a-2, 3$ or 4 denotes $C_2P_3D(a)$, $t-C_2P_2D_2(a)$, $c-C_2P_2D_2(a)$, $a-C_2P_2D_2(a)$, $C_2PD_3(a)$ or $C_2D_4(a)$ respectively. The values of α and β are adjusted according to the equations (4.a), (9.y) and (9.A,B) to the experimental results of FLANAGAN and RABINOVITCH with satisfactory agreements, as shown in Table I, between calculated and observed relative values of initial formation rates of C_2P_4D etc., i.e. the ratio of V^{C_2P} , etc.

TABLE I. Observed and calculated relative values of the initial formation rates $V^{C_2P_4}$, etc. of deuterioethylenes from trans-dideuterioethelene at 7.4 cmHg and 75°C on nickel.

Parameters adjusted			Relative values of initial formation rates, %							
Parameters	α	β	Remark	Deuterioethylenes					C_2PD_3	C_2D_4
				C_2P_4	C_2P_3D	$C_2P_2D_2$				
						trans	cis	asym.		
Adjusted values	6×10^{-2}	1×10^{-1}	obs.	0.3	18.5	-100.0	62.0	0.7	18.5	0.8
			calc.	0.15	25.2	-100.0	47.9	0.3	25.2	0.15

ii) The exchange reaction between light and tetradeutero-ethylene at 153°C.

The analysis has shown that both α and β are vanishingly small compared with unity or, according to (7.a) and (7.β), I is practically in the exchange equilibrium. Identifying in consequence $y^{C_2P_4(a)}$ etc. or $V^{C_2P_4(a)}$ etc. with $y^{C_2P_4}$ etc. or $V^{C_2P_4}$ etc. respectively and putting rates $V^{C_2P_4}$ etc. of intermediates $P_2C^* - CP_3$ etc. individually zero for the steady state, we have from Eqs. (4.b), (4.c), (5), (8) and the initial conditions, i.e. $y^{C_2P_4} = y^{C_2D_4} = \frac{1}{2}$ and $y^{C_2P_3D} = y^{t-C_2P_2D_2} = y^{c-C_2P_2D_2} = y^{a-C_2P_2D_2} = y^{C_2PD_3} = 0$,

$$\left. \begin{aligned} V^{C_2P_4}/V(II_a) = V^{C_2D_4}/V(II_a) &= -\frac{1}{6} - \frac{7\beta}{16\alpha} \\ V^{C_2P_3D}/V(II_a) = V^{C_2PD_3}/V(II_a) &= \frac{1}{6} + \frac{\beta}{4\alpha} \\ (V^{t-C_2P_2D_2} + V^{c-C_2P_2D_2} + V^{a-C_2P_2D_2})/V(II_a) &= 3\beta/8\alpha. \end{aligned} \right\} \quad (10)$$

TABLE II. Observed and calculated relative values of the inial formation rates $V^{C_2P_4}$, $V^{C_2P_3D}$ etc. from 1:1 mixture of light and tetradeutero-ethylene each of 3.8 cmHg partial pressure at 153°C on nickel.

Parameter adjusted		Relative values of initial formation rates, %					
Parameter	β/α	Remark	Deuterioethylenes				
			C_2P_4	C_2P_3D	$C_2P_2D_2$ total	C_2PD_3	C_2D_4
Adjusted value	2.6×10^{-2}	obs.	- 50.0	48.0	4.0	48.0	- 50.0
		calc.	- 50.0	48.6	2.7	48.6	- 50.0

The relative values of $V^{C_2P_4}$, etc. calculated from the value 0.026 of β/α adjusted to the experimental values are shown in Table II in comparison with the latter.

§ 3. Discussion

The experimental results of FLANAGAN and RABINOVITCH are quantitatively interpreted on the basis of the Scheme (1) without resorting to the improbable assumption referred to in the introduction.

The ratio $V(II_b)/V(II_a)$ is 0.0018 or 0.026 at 75°C or 153°C respectively as computed from the values of parameters given in Tables I and II, i. e. it decreases with decreasing temperature. The ratio $V(I)/\{V(I)+V(II_a)+V(II_b)\}$ decreases on the other hand with decreasing temperature from unity at 153°C, as follows from the exchange equilibrium of I concluded in §2 ii), to 0.94*⁾ at 75°C as calculated from the values of parameters given in Table I.

These ratio may hence be appreciably smaller than unity at sufficiently low temperatures, so that $V(II_b)$ as well as $V(I)$ is negligibly small compared with $V(II_a)$. It follows now according to the Scheme (1) that the exchange reaction proceeds principally through II_a and I, with the rate controlled by the latter resulting in the 'random distribution', i. e.

$$y^{C_2P_4-nD_n} = \frac{4!}{n!(4-n)!} (y^I)^{4-n} (y^D)^n \quad (n \leq 4) \quad (11)$$

or according to (4.a) and (8), in an experimentally verifiable conclusion

$$V^{C_2P_4-nD_n} = V(I) \left(\frac{3}{2 \cdot n!(4-n)!} - y^{C_2P_4-nD_n} \right), \quad (n \leq 4) \quad (12)$$

where $y^{C_2P_4-nD_n} (n \leq 4)$ depends on the initial condition of the experiment.

*) This value of $V(I)/\{V(I)+V(II_a)+V(II_b)\}$ is sensibly discriminated from unity which leads to the negative value of the essentially positive quantity β/α , when adjusted to the observed values of $V^{C_2P_4D_2}$, $V^{C-C_2P_2D_2}$ or $V^{t-C_2P_2D_2}$ according to the rate equations

$$\left. \begin{aligned} V^{C_2P_4D_2}/V(II_a) &= \frac{1}{6} + \frac{\beta}{4\alpha} \\ V^{C-C_2P_2D_2}/V(II_a) &= \frac{1}{6} + \frac{\beta}{16\alpha} \\ V^{t-C_2P_2D_2}/V(II_a) &= -\frac{1}{6} - \frac{13\beta}{16\alpha} \end{aligned} \right\}$$

which are derived similarly as in §2 ii) for the exchange equilibrium of the step I in accordance with unity of the value.

It will now be shown that the rate equations put forward by FLANAGAN and RABINOVITCH¹⁾ without giving theoretical grounds are derived from the Scheme (2.R) but not generally from the Scheme (2.A). According to the Scheme (2.R), V^{C_2P} , etc. are given respectively by $V^{C_2P,(a)}$ etc. of (4.b), with $y^{C_2P,(a)}$ etc. and $V(II_a)$ there respectively substituted by y^{C_2P} etc. and $V(II_a)$, neglecting the terms implying $V(II_b)$ in accordance with the absence of the step II_b in the Scheme (2.R)*, whereas the appropriate steady state condition is provided by (4.c) with the similar substitutions as those in (4.b) putting rates V^{C_2P} , etc. of intermediates P_2C-CP_3 etc. individually zero; noting further that $y^r + y^p = 1$, we have thus

$$\left. \begin{aligned} V^{C_2P}/V(II_a) &= \frac{1}{6} y^{C_2P_2D} y^r - \frac{2}{3} y^{C_2P} y^p \\ V^{C_2P_2D}/V(II_a) &= \frac{2}{3} y^{C_2P} y^p + \frac{1}{3} (y^{C-C_2P_2D_2} + y^{C-C_2P_2D_2}) y^r \\ &\quad + \frac{1}{3} y^{C-C_2P_2D_2} y^p - \left(\frac{1}{6} y^r + \frac{1}{3} y^p + \frac{1}{6} y^p \right) y^{C_2P_2D} \\ (V^{C-C_2P_2D_2} + V^{C-C_2P_2D_2})/V(II_a) &= \frac{1}{3} y^{C_2P_2D} y^p + \frac{1}{3} y^{C_2P_2D} y^r \\ &\quad - \left(\frac{1}{3} y^r + \frac{1}{3} y^p \right) (y^{C-C_2P_2D_2} + y^{C-C_2P_2D_2}) \\ &\dots \dots \dots \end{aligned} \right\} \quad (13)$$

which give just the rate equations given by FLANAGAN and RABINOVITCH

$$\left. \begin{aligned} dC^{C_2P}/dt &= k_H(C-D)_1 C^{C_2P_2D} C^r - 2k_D(C-H)_1 C^{C_2P} C^p \\ dC^{C_2P_2D}/dt &= 2k_D(C-H)_1 C^{C_2P} C^p + 2k_H(C-D)_1 (C^{C-C_2P_2D_2} \\ &\quad + C^{C-C_2P_2D_2}) C^r + k_H(C-D)_2 C^{C-C_2P_2D_2} C^r \\ &\quad - \{k_H(C-D)_1 C^r + k_D(C-H)_1 C^p + k_D(C-H)_2 C^p\} C^{C_2P_2D} \\ d(C^{C-C_2P_2D_2} + C^{C-C_2P_2D_2})/dt &= k_D(C-H)_1 C^{C_2P_2D} C^p + k_H(C-D)_2 C^{C_2P_2D_2} C^r \\ &\quad - \{2k_H(C-D)_1 C^r + 2k_D(C-H)_2 C^p\} (C^{C-C_2P_2D_2} + C^{C-C_2P_2D_2}) \\ &\dots \dots \dots \end{aligned} \right\} \quad (14)$$

(t: time)

by replacing y^r or y^{C_2P} , etc. with the concentration C^r or C^{C_2P} , etc. of P^* or C_2P_1 etc. respectively and coefficients 1/6, 1/3, 1/3 and 1/6 respectively

*) Terms implying $V(I)$ vanish at the replacement of $y^{C_2P,(a)}$ etc. by y^{C_2P} , etc. respectively.

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with $k_H(\text{C-D})_1$, $k_D(\text{C-H})_1$, $k'_H(\text{C-D})_2$ and $k'_D(\text{C-H})_2$ in accordance with their system of notation. On the basis of the Scheme (2.A), on the other hand, the rate equations (13) result in the case of the exchange equilibrium of I, when (2.A) is kinetically identical with (2.R) and II_a with II'_a , but not generally as seen from the random distribution of (12), which is incompatible with (2.R)*), in the extreme case when the exchange reaction is controlled by I.

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*) The random distribution is attained in this case only at the final stage of the reaction when (2.R) is in the exchange equilibrium.