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Title	RATES OF DIFFERENT DEUTEROETHYLENE AND DEUTEROETHANE FORMATION DURING CONTACT DEUTERATION OF LIGHT ETHYLENE IN THE PRESENCE OF NICKEL CATALYST : Explanation to TURKEVICH, SCHISSLER and IRSA's Experiment and Theoretical Predictions
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RATES OF DIFFERENT DEUTEROETHYLENE AND DEUTEROETHANE FORMATION DURING CONTACT DEUTERATION OF LIGHT ETHYLENE IN THE PRESENCE OF NICKEL CATALYST

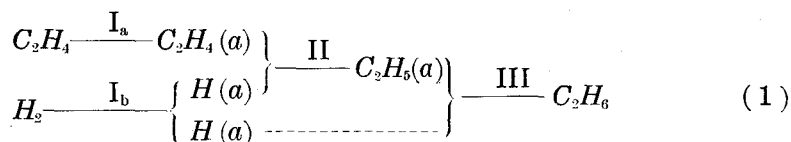
Explanation to TURKEVICH, SCHISLER and IRSA's
Experiment and Theoretical Predictions

By

Tominaga KEIJI

Introduction

FARKAS, FARKAS and RIDEAL¹⁾ found that the catalysed interaction of hydrogen^{*)} and ethylene both of ca. 10 mm Hg partial pressure at 120°C in the presence of nickel catalyst is accompanied by a rapid exchange of hydrogen atoms between the reaction partners. HORIUTI and POLANYI²⁾ observed similar exchange reactions between hydrogen and benzene, water and ethylene and water and benzene in the presence of nickel or platinum catalyst and put forward on the basis of these experiments inclusive of FARKAS, FARKAS and RIDEAL's one, the scheme,



of contact hydrogenation of ethylene involving the exchange reaction.

The scheme (1) represents the following sequence of elementary reactions. Ethylene C_2H_4 and hydrogen H_2 in gas are respectively adsorbed in Steps I_a and I_b to form adsorbed ethylene $C_2H_4(a)$, the two

*) Word "hydrogen" and notation "H" will be used colligatively for protium and deuterium, not particularly for the former, to which notation P will be appropriate throughout. Word "hydrogenation" will similarly cover hereafter the addition of deuterium and protium respectively. Ethylene C_2H_4 will stand for light ethylene C_2P_4 , deuterioethylenes C_2P_3D etc. and ethane C_2H_6 will similarly.

1) FARKAS, FARKAS and RIDEAL, Proc. Roy. Soc., **146**, 630, (1934).

2) HORIUTI and POLANYI, Trans. Faraday Soc., **30**, 1164, (1934).

carbon atoms being bonded each to one point on the catalyst, and dissociated pair of adsorbed hydrogen atoms $H(a)$'s respectively. The $C_2H_4(a)$ then picks up $H(a)$ in Step II to form adsorbed ethyl group $C_2H_5(a)$ or half-hydrogenated state as called by HORIUTI and POLANYI,⁽²⁾ which is linked at one point on the catalyst by its methylene group, three hydrogen atoms inclusive of the picked up one, of the methyl group linked to the latter being chemically equivalent to each other.

Hydrogenation is completed if $C_2H_5(a)$ picks up another $H(a)$ in Step III, whereas the exchange alternatively results in, if the reversal of II occurs to it, giving off one of two native hydrogen atoms to form $H(a)$, being followed by the reversals of I_a and I_b .

Associative mechanism of HORIUTI and POLANYI⁽²⁾ is that of Scheme (1) with the rate-determining step of III. They could account for FARKAS, FARKAS and RIDEAL's result mentioned above as well as their own but not another result of the latter group of authors, that the exchange was imperceptible at 20°C, besides at the same conditions as those of the above experiment, notwithstanding the steady progress of the hydrogenation.

HORIUTI⁽³⁾ developed later the "structure" theory of reaction, expressing the overall rate, the associated exchange reaction rate etc. in terms of statistical-mechanical functions appropriate to respective elementary reactions. The function, the reaction rate of the elementary reaction as called by him, is of the physical meaning of the overall reaction rate, which would be revealed, if all elementary reactions except the relevant one were balanced or at equilibrium.

The theory was first applied to the catalysed hydrogenation of ethylene,



on the basis of Scheme (1) but not adhering to the rate-determining step of III. All but one constant in the function of every elementary reaction was calculated statistical-mechanically from spectroscopic data of gaseous molecules, H_2 , C_2H_4 and C_2H_6 , the latter being estimated theoretically or fitted to experiment. The "structure" of reaction (2) thus being established, all conclusions derived from it was found to fit in with existing data: the existence of optimum temperature for the hydrogenation rate, for instance, was explained, its position at a given ethylene and hydrogen partial pressures being quantitatively

3) HORIUTI, Catalyst 2, (1948) 1.

predicted.

TURKEVICH, SCHISLAR and IRSA⁴⁾ have recently observed rates of different ethylenes, C_2P_3D , $C_2P_2D_2$ etc. and different ethanes C_2P_6 , C_2P_4D etc. in the course of interaction of D_2 with C_2P_4 respectively of 20 and 10 mmHg partial pressure at 90°C in the presence of nickel catalyst by means of the massspectrometer and obtained an important result that the initial rate of different ethylenes and ethanes formation decreases regularly with increasing deuterium substitution, ethanes formed initially being predominately C_2P_6 . They remark the result of predominant C_2P_6 formation surprising but this is rather a necessary consequence of the "structure" theory as shown below.

The theory concludes with regard to their particular experimental condition of 10 mmHg (C_2P_4) and 20 mmHg (D_2) partial pressures that,

A) the optimum temperature lies at 130°C,

B. L) below the optimum, $\bar{v}(I_b) \ll \bar{v}(I_b) \simeq \bar{v}(III) \ll \bar{v}(II) \simeq \bar{v}(II)$,

B. H) above the optimum, $\bar{v}(III) \ll \bar{v}(II) \simeq \bar{v}(II) \ll \bar{v}(I_b) \simeq \bar{v}(I_b)$,

and either below or above it commonly,

C. i) $\bar{v}(r), \bar{v}(r) \ll \bar{v}(I_a) \simeq \bar{v}(I_a)$, where $r = I_b, II$ and III , and,

C. ii) $\bar{v}(III) \ll \bar{v}(III) \ll \bar{v}(II) \simeq \bar{v}(II)$,

where $\bar{v}(I_b), \bar{v}(I_b)$ etc. denote the forward and backward rates of I_b etc. ... B. L) implies the rate-determining step of I_b , whereas B. H) that of III . The "structure" hence conforms with the earlier associative mechanism above the optimum but not below.

As the temperature of their experiment was below the optimum, $H(a)$ once formed from H_2 gets, according to (B. L) frequently into $C_2H_4(a)$ by II rather than into C_2H_6 by III or back into H_2 by the reversal of I_b . But since $C_2H_4(a)$ and C_2H_4 are quickly converting to each other according to C. i), $H(a)$ originates practically from C_2H_4 , i.e. it consists predominantly of $P(a)$, $D(a)$ formed from D_2 being instantly replaced by $P(a)$ from C_2P_4 . The result is the predominant formation of C_2P_6 as observed.

It is the purpose of the present paper to extend the theory with regard to the individual deuterium-substituted compound or develop the "fine structure" of the reaction for explaining their results more closely and deriving some theoretical predictions yet to be verified.

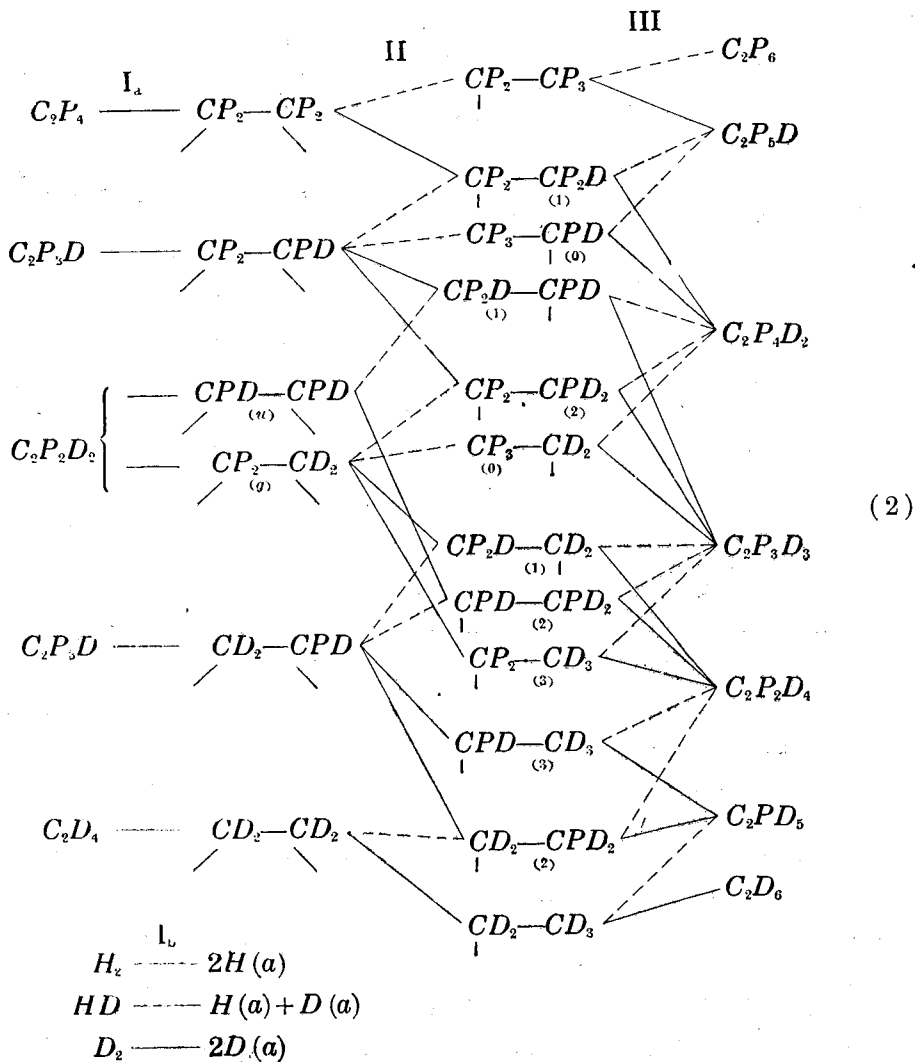
It is assumed in what follows that the isotopic replacement does not alter the rate of any elementary reaction, that the steady state is

4) TURKEVICH, SCHISLAR and IRSA, J. Phys.-Colloid Chem., 55, 1078, (1951).

established with respect to the intermediate product $C_2H_4(a)$, $H(a)$ and $C_2H_5(a)$ and that we are concerned with the initial stage, when C_2H_4 and H_2 consists practically of C_2P_4 and D_2 respectively and no ethane whatever practically exists.

§1. Rates of Formation of Individual Deuterocompounds

Scheme (1) appears, if written with distinction of individual deuterocompound as,



where dotted or full line denotes the transition involving $P(a)$ or $D(a)$ respectively, symbol g discriminates one of the two structural isomers of more even distribution of deuterium between the two carbon atoms from the other denoted by u .

Denoting j -th deuterium substitution product of molecule δ , for instance D_2 or PD of $\delta \equiv H_2$, by δ_j , the increasing rate \dot{Y}^{δ_j} of δ_j 's in gas, which is subject to the mass-spectral analysis, is expressed as,

$$\left. \begin{aligned} \dot{Y}^{P_2} &= \bar{v}(I_b) (y^{P(a)})^2 - \bar{v}(I_b) y^{P_2} \\ \dot{Y}^{PD} &= 2\bar{v}(I_b) y^{P(a)} y^{D(a)} - \bar{v}(I_b) y^{PD} \quad *) \\ \dot{Y}^{D_2} &= \bar{v}(I_b) (y^{D(a)})^2 - \bar{v}(I_b) y^{D_2} \end{aligned} \right\} \quad (3)$$

$$\left. \begin{aligned} \dot{Y}^{C_2P_4} &= \bar{v}(I_a) y^{C_2P_4(a)} - \bar{v}(I_a) y^{C_2P_4} \\ \dots\dots\dots & \\ \dots\dots\dots & \end{aligned} \right\} \quad (4)$$

$$\left. \begin{aligned} \dot{Y}^{C_2P_6} &= \bar{v}(III) y^{C_2P_6(a)} y^{P(a)} - \bar{v}(III) y^{C_2P_6} \\ \dots\dots\dots & \\ \dots\dots\dots & \end{aligned} \right\} \quad (5)$$

where y^{δ_i} is the fraction of the number of δ_i over the total number of δ .

§2. Steady State Conditions

Equating the rate of consumption to that of formation of individual intermediate products, steady state conditions are obtained as below:

$$\begin{aligned} \left\{ 2\bar{v}(I_b) + \bar{v}(II) + \bar{v}(III) \right\} y^{D(a)} &= \bar{v}(I_b) \left\{ 2y^{D_2} + y^{PD} \right\} + \bar{v}(II) \left\{ \frac{1}{3} y^{C_2P_4(a,1)} \right. \\ &+ \frac{2}{3} y^{C_2P_2D_2(a,2)} + y^{C_2P_2D_3(a,3)} + \frac{1}{3} y^{C_2P_3D_2(a,1)} + \frac{2}{3} y^{C_2P_2D_3(a,2)} + y^{C_2PD_4(a,3)} \\ &+ \frac{1}{3} y^{C_2P_2D_3(a,1)} + \left. \frac{2}{3} y^{C_3PD_4(a,2)} + y^{C_2D_5(a)} \right\} + \bar{v}(III) \left\{ \frac{1}{6} y^{C_2P_6D} + \frac{1}{3} y^{C_2P_4D_2} \right. \\ &+ \left. \frac{1}{2} y^{C_2P_3D_3} + \frac{2}{3} y^{C_2P_2D_4} + \frac{5}{6} y^{C_2PD_6} + y^{C_2D_6} \right\} \end{aligned} \quad (7)$$

for $D(a)$,

*) The factor 2 on the right-hand side accounts for the fact that $y^{P(a)}y^{D(a)}$ gives the probability of prescribed one of the two combining atoms being exclusively either deuterium or protium: the alternative case contributes the same, resulting in the factor.

$$\left. \begin{aligned}
 & \left\{ \bar{v}(\text{I}_a) + \bar{v}(\text{II}) \right\} y^{C_2P_4(a)} = \bar{v}(\text{I}_a) y^{C_2P_4} + \bar{v}(\text{II}) \left\{ y^{C_2P_3(a)} + \frac{1}{3} y^{C_2P_4D(a,1)} \right\} \\
 & \left\{ \bar{v}(\text{I}_a) + \bar{v}(\text{II}) \right\} y^{C_2P_3D(a)} = \bar{v}(\text{I}_a) y^{C_2P_3D} + \bar{v}(\text{II}) \left\{ y^{C_2P_4D(a,0)} \right. \\
 & \quad \left. + \frac{2}{3} y^{C_2P_4D(a,1)} + \frac{1}{3} y^{C_2P_3D_2(a,1)} + \frac{2}{3} y^{C_2P_3D_2(a,2)} \right\} \\
 & \dots\dots\dots \\
 & \left\{ \bar{v}(\text{I}_a) + \bar{v}(\text{II}) \right\} y^{C_2D_4(a)} = \bar{v}(\text{I}_a) y^{C_2D_4} + \bar{v}(\text{II}) \left\{ \frac{1}{3} y^{C_2PD_4(a,2)} + y^{C_2D_5(a)} \right\}
 \end{aligned} \right\} \quad (8)$$

for $C_2H_4(a)$'s respectively and,

$$\left. \begin{aligned}
 & \left\{ \bar{v}(\text{II}) + \bar{v}(\text{III}) \right\} y^{C_2P_5(a)} = \bar{v}(\text{II}) y^{C_2P_4(a)} y^{P(a)} + \bar{v}(\text{III}) \left\{ y^{C_2P_5} + \frac{1}{6} y^{C_2P_5D} \right\} \\
 & \left\{ \bar{v}(\text{II}) + \bar{v}(\text{III}) \right\} y^{C_2P_4D(a,1)} = \bar{v}(\text{II}) \left\{ y^{C_2P_4(a)} y^{P(a)} + \frac{1}{2} y^{C_2P_3D(a)} y^{P(a)} \right\} \\
 & \quad + \bar{v}(\text{III}) \left\{ \frac{5}{6} y^{C_2P_5D} + \frac{1}{3} y^{C_2P_4D_2} \right\} \\
 & \dots\dots\dots \\
 & \left\{ \bar{v}(\text{II}) + \bar{v}(\text{III}) \right\} y^{C_2D_5(a)} = \bar{v}(\text{II}) y^{C_2D_4(a)} y^{D(a)} + \bar{v}(\text{III}) \left\{ \frac{1}{6} y^{C_2PD_5} + y^{C_2D_6} \right\}
 \end{aligned} \right\} \quad (9)$$

for $C_2H_5(a)$'s respectively.

§ 3. Specialization to the Initial Condition

Putting,

$$y^{C_2P_4} = y^{D_2} = 1, \quad y^{P_3} = y^{PD} = 0, \quad y^{C_2P_5} = y^{C_2P_5D} = \dots = y^{C_2D_5} = 0 \quad (10)$$

in (3), (4), (5), (8) and (9) along with the initial condition of the TURKEVICH, SCHILLER and IRSA's reaction and eliminating $y^{C_2D_4(a)}$, $y^{C_2P_3D(a)}$, ... $y^{C_2D_4(a)}$, $y^{C_2P_5(a)}$, $y^{C_2P_4D(a,1)}$... $y^{C_2D_5(a)}$ from them, remembering the relation $y^{P(a)} + y^{D(a)} = 1$, we have,

$$\dot{Y}^{P_2} : \dot{Y}^{PD} = 1 : 2\Omega, \quad (11. Y)$$

where $\Omega = y^{D(a)}/1 - y^{D(a)}, \quad (11. \Omega)$

$$\dot{Y}^{C_2P_4} = \bar{v}(\text{I}_a) \left[-1 + \left\{ \frac{\bar{v}(\text{I}_a) R_1}{\dot{\alpha} y^{D(a)}} / 1 - (R_1 R_1' / 9\Omega) \right\} \right] \quad (12. H)$$

$$\begin{aligned}\dot{Y}^{C_2P_3D} &= \frac{2}{3} R_1' \{ \dot{Y}^{C_2P_3} + \bar{v}(I_a) \} = \dot{Y}^{C_2P_2D_2} / \frac{1}{2} R_2' \\ &= \dot{Y}^{CPD_3} / \frac{1}{6} R_2' R_3' = \dot{Y}^{C_2D_4} / \frac{1}{36} R_2' R_3' R_4'\end{aligned}\quad (12. D)$$

where

$$\left. \begin{aligned}R_1' &= R / 1 - (R_1 R_2 / 6\Omega) \\ R_2' &= R_2 / 1 - (R_2 R_3 / 6\Omega) \\ R_3' &= R_3 / 1 - (R_3 R_4 / 9\Omega) \\ R_1 &= \alpha y^{D(a)} / \left\{ \bar{v}(I_a) + \bar{v}(II) - \alpha \left(1 - \frac{2}{3} y^{D(a)} \right) \right\} \\ R_2 &= \alpha y^{D(a)} / \left\{ \bar{v}(I_a) + \bar{v}(II) - \frac{2}{3} \alpha \right\} \\ R_3 &= \alpha y^{D(a)} / \left\{ \bar{v}(I_a) + \bar{v}(II) - \frac{1}{2} \alpha \left(1 + \frac{2}{3} y^{D(a)} \right) \right\} \\ R_4 &= \alpha y^{D(a)} / \left\{ \bar{v}(I_a) + \bar{v}(II) - \frac{1}{3} \alpha \left(1 + 2 y^{D(a)} \right) \right\}\end{aligned}\right\} \quad (12. R)$$

$$\alpha = \bar{v}(II) \bar{v}(III) / \{ \bar{v}(II) + \bar{v}(III) \} \quad (12. \alpha)$$

$$\begin{aligned}\dot{Y}^{C_2P_3} &= \dot{Y}^{C_2P_3D} / \left(2\Omega + \frac{2}{3} R_1' \right) = \dot{Y}^{C_2P_4D_2} / \left\{ \Omega^2 + \frac{2}{3} R_1' \left(2\Omega + \frac{1}{3} R_2' \right) \right\} \\ &= \dot{Y}^{C_2P_3D_3} / \frac{2}{3} R_1' \left\{ \Omega^2 + \frac{1}{2} R_2' \left(2\Omega + \frac{1}{3} R_3' \right) \right\} \\ &= \dot{Y}^{C_2P_2D_4} / \frac{1}{3} R_1' R_2' \left\{ \Omega^2 + \frac{1}{3} R_3' \left(2\Omega + \frac{1}{9} R_4' \right) \right\} \\ &= \dot{Y}^{C_2P_2D_4} / \frac{1}{9} R_1' R_2' R_3' \left\{ \Omega^2 + \frac{1}{3} R_4' \Omega \right\} = \dot{Y}^{C_2D_6} / \frac{1}{54} R_1' R_2' R_3' R_4' \Omega^2\end{aligned}\quad (13)$$

and,

$$y^{D(a)} = \frac{2\bar{v}(I_b) + \frac{\alpha}{9} R_1' \left\{ 1 + R_2' + \frac{1}{2} R_2' R_2' + \frac{1}{6} R_2' R_3' R_4' \right\}}{2\bar{v}(I_b) + \bar{v}(II) + \bar{v}(III) - \frac{\alpha}{3}} \quad (14)$$

§ 4. Further Specialization

Above conclusions (11), (12), (13) and (14) are further specialised first to the experimental condition characterised by C.i), C.ii).

We have immediately from (12. α) and C.ii),

$$\alpha \simeq \bar{v}(\text{II}) \quad (15)$$

on one hand and from (12. R) and C. i) noting that $y^{D(\alpha)} \leq 1$,

$$R_1 \simeq R_2 \simeq R_3 \simeq R_4 \simeq R \ll 1 \quad (16. R_i)$$

where,

$$R \equiv y^{D(\alpha)} \bar{v}(\text{II}) / \bar{v}(\text{I}_a) \quad (16. R)$$

on the other hand.

We have now according to (16. R_i), (16. R), (11. Ω) and C. i),

$$R_3 R_4 / \Omega = R^2 / \Omega = y^{D(\alpha)} (1 - y^{D(\alpha)}) (\bar{v}(\text{II}) / \bar{v}(\text{I}_a))^2 \ll 1 \quad (17. a)$$

$$R / \Omega = (1 - y^{D(\alpha)}) \bar{v}(\text{II}) / \bar{v}(\text{I}_a) \ll 1 \quad (17. b)$$

and henceforth according to (12. R)

$$R'_i \simeq R_i \simeq R, \quad i = 1, 2, 3, 4. \quad (18)$$

It follows now from (18) and (12. D),

$$\dot{Y}^{C_2P_3D} : \dot{Y}^{C_2P_2D_2} : \dot{Y}^{C_2P_3D_3} : \dot{Y}^{C_2D_4} = 1 : R/2 : R^2/6 : R^3/36 \quad (19. C_2P_4)$$

and from (13), (18) and (17. b),

$$\begin{aligned} \dot{Y}^{C_2P_6} : \dot{Y}^{C_2P_3D} : \dot{Y}^{C_2P_2D_2} : \dot{Y}^{C_2P_3D_3} : \dot{Y}^{C_2P_2D_4} : \dot{Y}^{C_2P_3D_6} : \dot{Y}^{C_2D_6} = \\ 1 : 2\Omega : \Omega^2 : \frac{2}{3} R \Omega^2 : \frac{1}{3} R^2 \Omega^2 : \frac{1}{9} R^3 \Omega^2 : \frac{1}{54} R^4 \Omega^2. \end{aligned} \quad (19. C_2P_6)$$

(19. C_2P_4) shows according to (16. R_i) that $\dot{Y}^{C_2P_3D}$ etc. should decrease with increasing deuterium substitution of ethylene as observed by TURKEVICH, SCHISLER and IRSA,⁽⁴⁾ whereas relative magnitude of $\dot{Y}^{C_2P_i}$'s and that of \dot{Y}^{P_i} 's as given respectively by (19. C_2P_6) and (11. Y) depends on Ω , which is expressed according to (11. Ω) (14), C. ii), (16. R_i) and (18) as,

$$\Omega = \bar{v}(\text{I}_b) / \left\{ \bar{v}(\text{I}_b) - \bar{v}(\text{I}_b) + \frac{1}{3} \bar{v}(\text{II}) \right\}. \quad (20)$$

Conclusions so far arrived at are equally valid either above or below the optimum temperature.

Specializing finally to the experimental condition of TURKEVICH, SCHISLER and IRSA⁽⁴⁾ of being below the optimum, we have immediately from the relevant relation B. L) and (20),

$$\Omega \simeq 3\bar{v}(\text{I}_b) / \bar{v}(\text{II}) \ll 1. \quad (21. L)$$

It follows from (19. C_2P_6), (16. R_i) and (21. L) that $\dot{Y}^{C_2H_6}$ decreases regularly with increasing substitution of deuterium, just as observed by the latter authors.

§ 5. Theoretical Predictions

We might now add a few theoretical predictions, which are valid at partial pressures of H_2 and C_2H_4 in the neighbourhood of those of the experiment of TURKEVICH, SCHISLER and IRSA⁽⁴⁾.

Above the optimum temperature, where B.H) is valid, we have immediately from (20),

$$\Omega \gg 1 \quad (21.H)$$

and hence from (11.Y) incorporating (21.L) that,

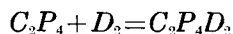
$$(a) \quad \dot{Y}^{P_2} < \dot{Y}^{PD} \text{ or } \dot{Y}^{P_2} > \dot{Y}^{PD}$$

according as the temperature is above or below the optimum.

On the other hand (21.H) and (19.C₂P₆) predicts that,

(b) $\dot{Y}^{C_2H_6}$ increases with increasing deuterium substitution as far as $C_2P_4D_2$ and then decreases with further substitution.

This conclusion, which a chemical equation,



written straightforward for the reaction might suggest, may be inferred by a qualitative reasoning as below. The "structure" of the reaction characterised by B.H), C.i) and C.ii) states that the narrowest pass on the course of communicating hydrogen atom from H_2 to C_2H_4 is II, $C_2H_4(a)$ and C_2H_4 on one hand $H(a)$ and H_2 on the other hand being respectively interchanged quickly with each other. It follows that $C_2H_4(a)$ has come most probably from C_2H_4 and $H(a)$ similarly from H i.e. that $C_2H_4(a)$ consists practically of $C_2P_4(a)$ whereas $H(a)$ of $D(a)$ and henceforth that $C_2H_5(a)$ or C_2H_6 formed consists predominantly of $C_2P_4D(a)$ or of $C_2P_4D_2$ respectively.

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