



Title	THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYST : . Explanation of KEMBALL's Experimental Results on Evolution Rates of Deuteroethylenes and Deuteroethanes in Course of Catalyzed Deuteration of Light Ethylene.
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 7(3), 197-209
Issue Date	1959-12
Doc URL	http://hdl.handle.net/2115/24707
Type	bulletin (article)
File Information	7(3)_P197-209.pdf



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THEORY OF HYDROGENATION OF ETHYLENE ON METALLIC CATALYST

IV. Explanation of KEMBALL's Experimental Results on Evolution Rates of Deuteroethylenes and Deuteroethanes in Course of Catalyzed Deute- ration of Light Ethylene.

By

K. MIYAHARA and Y. YATSURUGI^{*)}

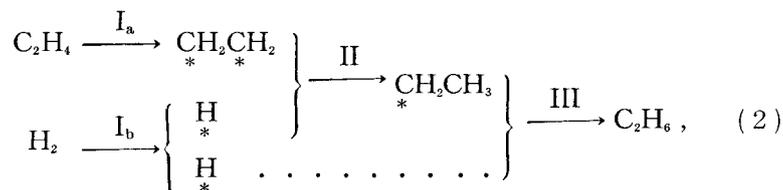
(Received December 28, 1959)

Introduction

It has been shown in Part I¹⁾ of this series that the rate of the catalyzed hydrogenation,



in the presence of metallic catalysts and those of associated reactions are given in terms of characteristic functions $\mathfrak{R}(s)$'s relevant each to the constituent step s of the associative mechanism²⁾ of the overall reaction (1),



i. e. I_a, I_b, II or III.

By associated reactions are meant so-called exchange reactions of hydrogen and ethylene, parahydrogen conversion, equilibration of hydrogen and evolution of different deuteroethylenes and deuteroethanes, which are going on along with the hydrogenation (1). The characteristic function $\mathfrak{R}(s)$ is the forward rate of step s at the steady state of hydrogenation multiplied by a factor $a_e^{I(s)}/a^{I(s)}$ of increase of the absolute activity of the relevant initial complex I(s) from its value $a^{I(s)}$ at the steady state to that $a_e^{I(s)}$ at equilibria of all steps but s ; $\mathfrak{R}(s)$ thus defined¹⁾³⁾ behaves like a rate constant as it reproduces the forward rate at the steady state when multiplied by the relevant relative activity $a^{I(s)}/a_e^{I(s)}$ of

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the initial complex, although not necessarily constant at a constant temperature but dependent in general upon the surface state of the catalyst.

Four $\mathfrak{K}(s)$'s have previously been statistical-mechanically formulated by HORIUTI³⁾ as reproduced in Part I¹⁾, under the assumption of bare and homogeneous catalyst's surface, as respective functions of partial pressures of reactants *i. e.* ethylene and hydrogen in gas and temperature, each with the appropriate activation energy $\Delta^*\epsilon(s)$ as a unique adjustable parameter. The latter being fitted to experiments or theoretically estimated¹⁾³⁾, a number of experimental results, inclusive of those advanced as evidences against the associative mechanism, have been semiquantitatively accounted for¹⁾³⁾.

The individual $\mathfrak{K}(s)$ could be determined, purely experimentally on the basis of the associative mechanism¹⁾³⁾⁴⁾, if there existed sufficient data, as functions of temperature and activities of adsorptives, which determine the surface state of the catalyst. Such functions, if determined at all, would enable us to find out some laws governing the individual constituent steps of the overall reaction to complete our knowledge of the heterogeneous reaction.

This being not at all the case at the present stage of our experimental knowledge, $\mathfrak{K}(s)$'s have been revised in Part II⁴⁾ allowing particularly for the effect of adsorbed hydrogen atoms for the first approximation, with reference to the experimental results of ZUR STRASSEN⁵⁾ and of TURKEVICH, SCHISLER and IRSA⁶⁾.

A number of experimental results have been deduced almost quantitatively from $\mathfrak{K}(s)$'s thus revised⁴⁾⁷⁾; among others, the excess activation energy of associated hydrogen exchange over that of hydrogenation has been deduced⁷⁾ quantitatively in agreement with the observation of TWIGG and RIDEAL⁸⁾, who based their argument⁸⁾⁹⁾ against the associative mechanism on the very result. HORIUTI and MATSUZAKI have deduced from them in Part III¹⁰⁾ the relations between the equilibrium fraction^{*}) u , the deuterium atomic fraction Y and partial pressure P^H of hydrogen in course of hydrogenation, which have reproduced the u, Y -relation observed by TWIGG and RIDEAL⁸⁾, who put forward the latter as another base of their argument against the associative mechanism on the one hand and predicted on the other hand a u, Y -relation at lower temperature, which contradicted the alternative mechanisms advanced by the latter authors⁸⁾⁹⁾ and a Y, P^H -relation yet to be observed.

MATSUZAKI¹¹⁾ has now experimentally verified above theoretical conclusions, establishing the associative mechanism and disproving the above alternative

*) The equilibrium fraction u is defined as the fraction of the amount of PD molecules (P: protium) present over that at equilibrium of reaction $P_2 + D_2 = PD$ of the hydrogen existing.

mechanisms⁸⁾⁹⁾. The revised $\mathfrak{K}(s)$'s have so far been demonstrated as valid around the temperature where they were fitted in with⁴⁾⁷⁾ the experimental results⁵⁾⁶⁾.

In terms of $\mathfrak{K}(s)$'s of the former crude estimation¹⁾³⁾, KEII¹²⁾ has already accounted for quantitatively the apparently puzzling experimental result of TURKEVICH, SCHISLER and IRSA⁶⁾ at 90°C, that light ethane was predominant among initial deuteration products of light ethylene catalyzed by nickel, the initial evolution rates of deuterioethanes decreasing with increase of deuterio substitution, and predicted on the same basis that the predominance shifts to dideuterioethane at sufficiently high temperature. KEMBALL¹³⁾ has however observed recently at a deep temperature of -100°C a peak of distribution of the similar deuteration products at monodeuterioethane instead at light ethane. This does not follow from the $\mathfrak{K}(s)$'s of the former crude estimation, which infers instead that the predominance of light ethane at higher temperature is simply amplified with decrease of temperature.

It is the purpose of the present paper to investigate whether the revised $\mathfrak{K}(s)$'s could reproduce the experimental results of KEMBALL at so low a temperature and, if at all, to draw some experimentally verifiable conclusions relevant to the latter experimental condition for further investigations. It may be noted that the relative evolution rates in question are decided by the relative values of $\mathfrak{K}(s)$'s as shown in Part II⁴⁾, hence not affected by any additional adsorptions at lower temperatures, in so far as they vary the absolute values of $\mathfrak{K}(s)$'s by the same factor⁴⁾.

Isotopic difference of rates is ignored throughout, and ethylene, hydrogen and ethane in gas are respectively denoted by E, H and A in what follows.

§ 1. Fundamental Analytical Relations

The steady condition of hydrogenation is stated in accordance with the associative mechanism as¹⁾³⁾

$$V_s = \bar{v}(s) - \tilde{v}(s), \quad s = I_a, I_b, II, III, \quad (3)$$

where V_s is the rate of the steady hydrogenation and $\bar{v}(s)$ or $\tilde{v}(s)$ the forward or the backward rate of step s . The latter is expressed in terms of $\mathfrak{K}(s)$ as¹⁾³⁾

$$\bar{v}(I_a) = \mathfrak{K}(I_a), \quad \tilde{v}(I_a) = \gamma(C_2H_4)\mathfrak{K}(I_a), \quad (4. I_a)$$

$$\bar{v}(I_b) = \mathfrak{K}(I_b), \quad \tilde{v}(I_b) = \gamma(H)^2\mathfrak{K}(I_b), \quad (4. I_b)$$

$$\bar{v}(II) = \gamma(C_2H_4)\gamma(H)\mathfrak{K}(II), \quad \tilde{v}(II) = \gamma(C_2H_5)\mathfrak{K}(II), \quad (4. II)$$

$$\bar{v}(III) = \gamma(C_2H_5)\gamma(H)\mathfrak{K}(III), \quad \tilde{v}(III) = \Gamma\mathfrak{K}(III), \quad (4. III)$$

where $\gamma(C_2H_4)$, $\gamma(H)$ or $\gamma(C_2H_5)$ is respectively the relative activity of an adsorbed

intermediate $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$, $\overset{*}{\text{H}}$ or $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_3$ at the steady state referred to its activity at the equilibrium of the intermediate with the reactants^{*)} *i. e.* **E** and **H**. Γ is the BOLTZMANN factor of the affinity of the hydrogenation (1) *i. e.*

$$\Gamma = \exp\left(\frac{\mu^{\text{A}} - \mu^{\text{E}} - \mu^{\text{H}}}{RT}\right), \quad (4. \Gamma)$$

where μ^{A} *etc.* are the chemical potentials of **A** *etc.* respectively, R is the gas constant and T the absolute temperature. Γ is calculated by (4. Γ) at 10^{-31} or less at the condition of the KEMBALL's experiment^{**) ,} on which ground $\bar{v}(\text{III})$ in (3) is ignored by (4. III) throughout in the present treatment as shown subsequently valid^{***)}.

Substituting $\bar{v}(s)$'s and $\bar{v}(s)$'s from (4) into (3), we have

$$\begin{aligned} V_s &= \mathfrak{K}(\text{I}_a)(1 - \gamma(\text{C}_2\text{H}_4)) = \mathfrak{K}(\text{I}_b)(1 - \gamma(\text{H})^2) = \mathfrak{K}(\text{II})(\gamma(\text{H})\gamma(\text{C}_2\text{H}_4) - \gamma(\text{C}_2\text{H}_6)) \\ &= \mathfrak{K}(\text{III})(\gamma(\text{H})\gamma(\text{C}_2\text{H}_6) - \Gamma). \end{aligned} \quad (5)$$

It follows from the condition $\Gamma < 1$ according to (5), that¹⁾

$$V_s > 0, \quad (6. V)$$

$$0 < \gamma(\text{C}_2\text{H}_4), \gamma(\text{H}), \gamma(\text{C}_2\text{H}_6) < 1, \quad (6. r)$$

$$0 < \frac{V_s}{1 - \Gamma} < \mathfrak{K}(s), \quad s = \text{I}_a, \text{I}_b, \text{II}, \text{III}, \quad (6. \mathfrak{K})$$

and that $V_s/(1 - \Gamma)$ approaches $\mathfrak{K}(r)$, as one $\mathfrak{K}(r)$ of $\mathfrak{K}(s)$'s gets smaller than all other $\mathfrak{K}(s)$'s and inverse. (6. r)

The step r is called the rate-determining stsp of hydrogenation, as $\mathfrak{K}(r)$ is sufficiently small compared with all other $\mathfrak{K}(s)$'s.

§ 2. $\mathfrak{K}(s)$'s

The revised functions of $\mathfrak{K}(s)$'s are¹⁾

) The equilibrium is $\text{E} = \overset{}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$, $\text{H} = \overset{*}{\text{H}}$ or $\text{E} + \text{H}/2 = \overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_3$.

) The Γ is expressed in accordance with the definition (4. Γ) as $P^{\text{A}}/K_P P^{\text{E}} P^{\text{H}}$ [cf. Part I (ref. 1)], where P^{A} *etc.* are partial pressures of **A *etc.* and $K_P = P_e^{\text{A}}/P_e^{\text{E}} P_e^{\text{H}}$ is the equilibrium constant of the overall reaction in terms of the values P_e^{A} *etc.* of P^{A} *etc.* at equilibrium. K_P is extrapolated at 100°C as $2.8 \times 10^{29} \text{ mmHg}^{-1}$ from the spectroscopically calculated values 4.2×10^{13} and $1.7 \times 10^8 \text{ mmHg}^{-1}$ respectively at 300°K and 400°K (recalculated into the specified unit from data given in LANDOLT "Tabellen" Erg. IIIc, p. 2622). It is calculated on this basis that Γ increases in course of hydrogenation at the experimental condition of KEMBALL from zero to $\Gamma = 1.2 \times 10^{-31}$ at twenty percent completion of the hydrogenation starting from partial pressures $P^{\text{E}} = 2.7 \text{ mmHg}$ and $P^{\text{H}} = 8.1 \text{ mmHg}$.

***) Cf. footnote *) on p. 204

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$$\log \mathfrak{K}(\text{I}_a) = \log \rho \frac{P^E}{Q_p^E} - \frac{\Delta^* \epsilon(\text{I}_a)}{2.30 RT}, \quad (7. \text{I}_a)$$

$$\log \mathfrak{K}(\text{I}_b) = \log \rho \frac{P^H}{Q_p^H} + 0.525 \log \frac{P^E}{Q_p^E} - \frac{\Delta^* \epsilon(\text{I}_b)}{2.30 RT}, \quad (7. \text{I}_b)$$

$$\log \mathfrak{K}(\text{II}) = \frac{1}{2} \log \frac{P^H}{Q_p^H} + \log \rho \frac{P^E}{Q_p^E} - \frac{\Delta^* \epsilon(\text{II})}{2.30 RT}, \quad (7. \text{II})$$

$$\log \mathfrak{K}(\text{III}) = \log \rho \frac{P^H}{Q_p^H} + \log \frac{P^E}{Q_p^E} - \frac{\Delta^* \epsilon(\text{III})}{2.30 RT}, \quad (7. \text{III})$$

where ρ is a constant*, P^E or P^H the partial pressure of **E** or **H** in mmHg, Q_p^E or Q_p^H the statistical-mechanical constant of the value

$$Q_p^E = 3.939 \times 10^{14} \text{ mmHg}, \quad Q_p^H = 1.057 \times 10^{10} \text{ mmHg}, \quad (8. \text{E}), (8. \text{H})$$

and $\Delta^* \epsilon(\text{I}_a)$ etc. are constant activation energies of the values,

$$\Delta^* \epsilon(\text{I}_a) = -2.200 \text{ Kcal}, \quad \Delta^* \epsilon(\text{I}_b) = 6.210 \text{ Kcal}, \quad (9. \text{I}_a), (9. \text{I}_b)$$

$$\Delta^* \epsilon(\text{II}) = 0.757 \text{ Kcal}, \quad \Delta^* \epsilon(\text{III}) = -5.000 \text{ Kcal}. \quad (9. \text{II}), (9. \text{III})$$

The absolute activity a^E or a^H of **E** or **H** is expressed statistical-mechanically as¹⁴⁾ $a^E = N^E/Q^E$ or $a^H = N^H/Q^H$, where N^E or N^H and Q^E or Q^H are respectively the concentration and the partition function expressed as

$$Q^E = \frac{(2\pi m^E kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 (2\pi I^E kT)^{3/2}}{S^E h^3} \cdot \prod_{j=1}^{12} \left\{ 1 - \exp\left(-\frac{h\nu_j^E}{kT}\right) \right\}^{-1} \cdot \exp\left(-\frac{\epsilon_0^E}{kT}\right), \quad (10. \text{E})$$

$$Q^H = \frac{(2\pi m^H kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I^H kT}{S^H h^2} \cdot \exp\left(-\frac{\epsilon_0^H}{kT}\right), \quad (10. \text{H})$$

where m^E or m^H , S^E or S^H and ϵ_0^E or ϵ_0^H are respectively the mass, the symmetry number and the energy of the ground state of **E** or **H**, I^H the moment of inertia of **H**, I^E the geometric mean of the three principal moments of inertia of **E** and ν_j^E the frequency of the j -th normal vibration of **E**.

Substituting $1333 P^E/kT$ or $1333 P^H/kT$ for N^E or N^H , we have $1333 P^E/kTQ^E$ or $1333 P^H/kTQ^H$ for the respective absolute activity. Replacing now T in the denominator of the latter expressions and those in the first two factors of Q^E and Q^H there by $T_N \exp(1 - T_N/T)$ and T in the vibrational partition function $\prod_{j=1}^{12} \left\{ 1 - \exp(-h\nu_j^E/kT) \right\}^{-1}$ simply by T_N , where T_N is a certain medium temperature in the temperature range of interest, we have for the absolute activities¹³⁾

*) The absolute value of this constant is not of significance in the present calculation, where the relative magnitudes of $\mathfrak{K}(s)$'s determine the relative evolution rates in question as mentioned in the introduction.

$$a^E = \frac{P^E}{Q_p^E} \exp\left(-\frac{\epsilon_0^E + 4RT_N}{RT}\right), \quad a^H = \frac{P^H}{Q_p^H} \exp\left(-\frac{\epsilon_0^H + 7/2 \cdot RT_N}{RT}\right), \quad (11. E), (11. H)$$

where

$$Q_p^E = \frac{kT_N}{1333} \frac{(2\pi m^E kT_N)^{3/2}}{h^3} \frac{8\pi^2 (2\pi I^E kT_N)^{3/2}}{S^E h^3} \prod_{j=1}^{12} \left\{1 - \exp\left(-\frac{h\nu_j^E}{kT_N}\right)\right\}^{-1} e^t, \quad (12. E)$$

$$Q_p^H = \frac{kT_N}{1333} \frac{(2\pi m^H kT_N)^{3/2}}{h^3} \frac{8\pi^2 I^H kT_N}{S^H h^2} \cdot e^{t/2}, \quad (12. H)$$

and $\epsilon_0^E + 4RT_N$ or $\epsilon_0^H + 7/2 \cdot RT_N$ is the enthalpy per mol of **E** or **H** at $T = T_N$.

Eq. (11) for the absolute activity is accurate in the neighbourhood of T_N , inasmuch as $T_N \exp(1 - T_N/T)$ substituted for T reproduces T , when we expand it with respect to $(T - T_N)/T_N$ to retain terms as far as the first order one, and the vibrational partition function is nearly unity^{*} and varies extremely slowly with temperature tending to unity with decrease of temperature. Eq. (7) is formally the similar transcription of the original statistical-mechanical equation derived from the latter by substituting $T_N \exp(1 - T_N/T)$ for T in the non-exponential factors, resulting expressions of $\Delta^* \epsilon(I_a)$ etc. of (9) being $\Delta^* \epsilon(I_a) = \epsilon^{*(I_a)} + RT_N - (\epsilon_0^E + 4RT_N)$, $\Delta^* \epsilon(I_b) = \epsilon^{*(I_b)} + RT_N - (\epsilon_0^H + 7/2 \cdot RT_N)$, $\Delta^* \epsilon(II) = \epsilon^{*(II)} + RT_N - (\epsilon_0^E + 4RT_N) - 1/2 \cdot (\epsilon_0^H + 7/2 \cdot RT_N)$ and $\Delta^* \epsilon(III) = \epsilon^{*(III)} + RT_N - (\epsilon_0^E + 4RT_N) - (\epsilon_0^H + 7/2 \cdot RT_N)$, where $\epsilon^{*(s)}$ is the energy per mol of critical complex $\ddot{*}(s)$ of step s . Numerical values of $\Delta^* \epsilon(s)$, except that of $\Delta^* \epsilon(I_a)^{**}$ were, however, directly fitted to experiments according to (7) with the values of Q_p^E and Q_p^H given by (8), which are calculated by (12) for $T_N = 373.15 \text{ K}^\circ$.

The calculation in question has now been made at the experimental condition of KEMBALL¹³⁾ at -100°C with constants given by (8) and (9), which might be questioned because of an appreciable difference of the temperature from the above value of T_N . We could of course carry through the calculation in question assuming ϵ_0^E , ϵ_0^H and $\epsilon^{*(s)}$ are respectively constant, without the above substitution of T . This "accurate" procedure does not make however much difference as shown later. Since the constancy of $\epsilon^{*(s)}$'s are not exactly assured, we should rather proceed to examine the validity of the wieldy expressions of (7) at lower temperatures themselves as trial functions.

*) The vibrational partition function of **E** is 1.108 at 100°C , while that of **H** is practically exactly unity.

**) The $\Delta^* \epsilon(I_a)$ was estimated theoretically by the above expression for $T_N = 373.15^\circ\text{K}$ (Ref. 1), not being practically fixed by experimental data except that $\ddot{*}(I_a)$ was extremely larger than other $\ddot{*}(s)$'s (cf. Ref. 4). Fig. 1 shows that $\ddot{*}(I_a)$ drawn there by the above theoretical estimation of $\Delta^* \epsilon(I_a)$ conforms with the latter conclusion.

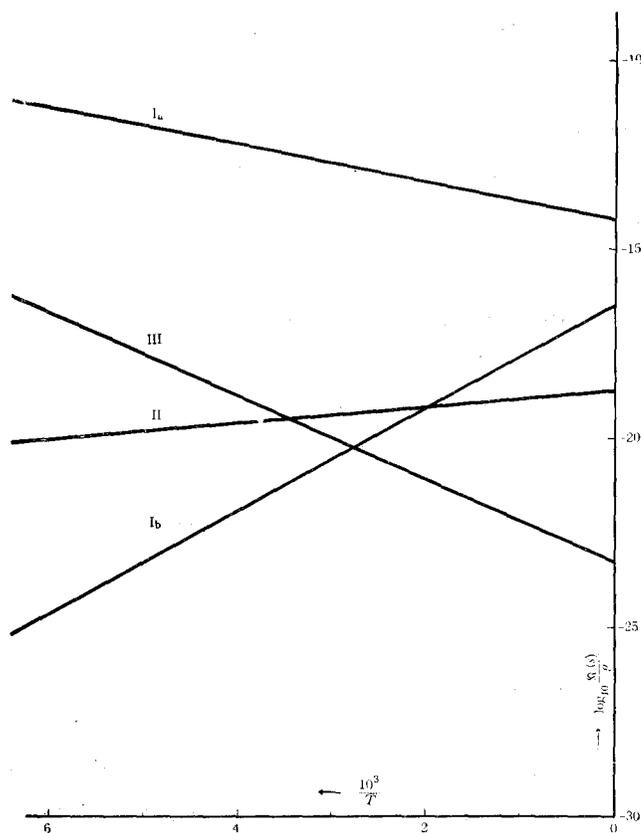


Fig. 1. $\log K(s)$'s of (7) versus $10^3/T$. $P^E=2.7$ mmHg, $P^H=8.1$ mmHg.

§ 3. Steady State of Hydrogenation

Fig. 1 shows the plot of $\log K(s)$'s given by (7) against $1000/T$ at the experimental condition of KEMBALL¹³⁾, where $P^E=2.7$ mmHg and $P^H=8.1$ mmHg. It is concluded from the extremely high $K(I_a)$ above other $K(s)$'s that $r(C_2H_4)$ equals practically unity with reference to (5) and (6. r), hence, according to (4), $\bar{v}(I_a)=\bar{v}(I_a)$, which are extremely large compared with other $\bar{v}(s)$'s and $\bar{v}(s)$'s, *i. e.*

$$r(C_2H_4)=1, \quad \bar{v}(I_a)=\bar{v}(I_a) \gg \bar{v}(s), \quad \bar{v}(s). \quad s=I_b, \text{ II, III.} \quad (13. a), (13. b)$$

It follows from (5) and (13. a) with neglect of Γ ,

$$K(I_b)(1-r(H)^2)=K(II)(r(H)-r(C_2H_5))=K(III)r(H)r(C_2H_5), \quad (14)$$

which gives on solving for $r(H)$ and $r(C_2H_5)$ for the condition of KEMBALL's experiment¹³⁾, where

$$\mathfrak{R}(\text{II})/\mathfrak{R}(\text{I}_b) = 5.26 \times 10^4, \quad \mathfrak{R}(\text{II})/\mathfrak{R}(\text{III}) = 1.91 \times 10^{-3} \quad (15. a), (15. b)$$

by (7), (8) and (9), that*

$$r(\text{H}) = 2.004 \times 10^{-4}, \quad r(\text{C}_2\text{H}_6) = 1.814 \times 10^{-4}. \quad (16. a), (16. b)$$

The relative rates of evolution of deuterioethylenes and deuterioethanes are now worked out in subsequent sections on the basis of the overall steady state of hydrogenation determined as above.

§ 4. Evolution Rates and Steady Condition for Individual Deuteriosubstituted Intermediates

The unidirectional evolution rate V^{E_l} of l -deuterioethylene E_l is given in accordance with the associative mechanism^{*)} as

$$V^{E_l} = x_l \bar{v}(\text{I}_a), \quad l = 0, 1, \dots, 4, \quad (17. E)$$

where x_l is the fraction of l -deuteriosubstituted $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$ over whole $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$ present. The similar rate V^{A_n} of n -deuterioethane A_n is given as

$$V^{A_n} = (y_1 z_{n-1} + y_0 z_n) \bar{v}(\text{III}), \quad n = 0, 1, \dots, 6, \quad (17. A)$$

where y_1 or y_0 is the fraction of $\overset{\text{D}}{\text{D}}$ or $\overset{\text{P}}{\text{P}}$ over whole $\overset{\text{H}}{\text{H}}$ present and z_n is the n -deuteriosubstituted $\overset{*}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_3$ over whole $\overset{\text{H}}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_3$ present, inasmuch as ethane is unidirectionally formed by the combination of $\overset{*}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_3$ and $\overset{\text{H}}{\text{H}}$ according to (2).

The steady condition for the individual deuteriosubstitution products of $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$ and $\overset{*}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_3$ is stated^{*)} assuming an equal distribution of deuterium over four hydrogen atoms of $\overset{\text{H}}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_2$ or of $\overset{\text{H}}{\text{C}}\text{H}_2\overset{\text{H}}{\text{C}}\text{H}_3$, which originate from $\overset{*}{\text{C}}\text{H}_2\overset{*}{\text{C}}\text{H}_2$, for the initial condition $X=0$ and $Y=1$, where X is the atomic fraction of deuterium over whole hydrogen atoms present in E, as

$$\left. \begin{aligned} \bar{v}(\text{I}_a) - x_0 \bar{v}(\text{I}_a) - x_0 \bar{v}(\text{II}) + \left(y_0 x_0 + \frac{1}{3} y_1 x_0 + \frac{1}{6} y_0 x_1 \right) \bar{v}(\text{II}) = 0, \quad l=0, \\ -x_l \bar{v}(\text{I}_a) - x_l \bar{v}(\text{II}) + \left\{ (5-l)y_1 x_{l-1} + (6-l)y_0 x_l + (2+l)y_1 x_l + (l+1)y_0 x_{l+1} \right\} \\ \times \frac{\bar{v}(\text{II})}{6} = 0, \quad l=1, \dots, 4, \end{aligned} \right\} \quad (18. E)$$

$$(y_1 x_{n-1} + y_0 x_n) \bar{v}(\text{II}) - z_n \bar{v}(\text{II}) - z_n \bar{v}(\text{III}) = 0, \quad n=0, \dots, 5. \quad (18. A)$$

*) The $r(\text{H})$ and $r(\text{C}_2\text{H}_6)$ are respectively very small compared with unity yet sufficiently large as regards Γ for $\bar{v}(\text{III})$ to be neglected in comparison with other $\bar{v}(s)$'s and $\bar{v}(s)$'s.

The steady condition for D_* or P_* is given respectively as

$$2\bar{v}(I_b) - 2y_1\bar{v}(I_b) - y_1\bar{v}(II) + (2X_1 + y_1)\bar{v}(II)/3 - y_1\bar{v}(III) = 0, \quad (18. D)$$

$$-2y_0\bar{v}(I_b) - y_0\bar{v}(II) + (2X_0 + y_0)\bar{v}(II)/3 - y_0\bar{v}(III) = 0, \quad (18. P)$$

where y_1 is the fraction of D_* over whole H_* present, X_0 or X_1 the atomic fraction of deuterium or protium in $CH_2CH_2_*$. We have by definition

$$\sum_{i=0}^4 x_i = X_0 + X_1 = y_0 + y_1 = \sum_{n=1}^5 z_n = 1, \quad X_1 = \sum_{l=1}^5 lx_l/4. \quad (19. a), (19. b)$$

Eqs.(18. E) give on summation from $l=0$ to $l=4$ with reference to (19. a)

$$\bar{v}(I_a) - \bar{v}(I_a) - \bar{v}(II) + \bar{v}(II) = 0. \quad (20. E)$$

The summation of (18. A) from $n=0$ to $n=5$ gives similarly

$$\bar{v}(II) - \bar{v}(II) - \bar{v}(III) = 0 \quad (20. A)$$

and that of (18. D) and (18. P)

$$2\bar{v}(I_b) - 2\bar{v}(I_b) - \bar{v}(II) + \bar{v}(II) - \bar{v}(III) = 0. \quad (20. H)$$

Eq.(20) follows however directly from the overall steady condition (3) with neglect of $\bar{v}(III)$.

Multiplying (18. E) now by l and summing the product up from $l=1$ to 4, we have, referring to (19)

$$-4X_1\bar{v}(I_a) - 4X_1\bar{v}(II) + \left(\frac{2}{3}y_1 + \frac{10}{3}X_1\right)\bar{v}(II) = 0,$$

which gives on eliminating $\bar{v}(I_a) + \bar{v}(II)$ from it and (20. E)

$$6X_1\bar{v}(I_a) = (y_1 - X_1)\bar{v}(II). \quad (21. E)$$

We have on the other hand by eliminating $2\bar{v}(I_a) + \bar{v}(II) + \bar{v}(III)$ from (18. D) and (20. H)

$$3(1 - y_1)\bar{v}(I_b) = (y_1 - X_1)\bar{v}(II) \quad (21. H)$$

or eliminating $\bar{v}(II) + \bar{v}(III)$ from (18. A) and (20. A)

$$y_1x_{n-1} + y_0x_n = z_n. \quad (21. A)$$

The relative evolution rates in question are deduced in subsequent sections from the above conclusions incorporated with the overall steady state of the reaction determined in § 3.

§ 5. Determination of Relative Evolution Rates

It follows from (13. b) and (21. E) that X_1 is extremely small compared with unity, hence by (19. b) the same is the case with x_l , $l=1, \dots, 4$, while according to (19. a), x_0 equals practically unity, *i. e.*,

$$X_1 \rightarrow 0, \quad x_{l(>0)} \rightarrow 0, \quad x_0 \rightarrow 1. \quad (22. a), (22. b), (22. c)$$

The product $x_l \bar{v}(I_a)$ of extremely small $x_{l(>0)}$ and large $\bar{v}(I_a)$ is evaluated by (18. E), (22. b) and (22. c) as $x_l \bar{v}(I_a) = \frac{2}{3} y_1 \bar{v}(II)$ or by (21. H) and (22. a)

$$x_l \bar{v}(I_a) = 2(1 - y_1) \bar{v}(I_b), \quad (23. a)$$

and

$$x_l \bar{v}(I_a) = 0, \quad l > 1. \quad (23. b)$$

It follows on the other hand from (21. A), (22. b) and (22. c),

$$z_0 = y_0, \quad z_1 = y_1, \quad z_2 = \dots = z_5 = 0. \quad (24)$$

Evolution rates of deuterioethylenes E's are given according to (17. E) and (23)

$$V^{E_1} = 2(1 - y_1) \bar{v}(I_b), \quad V^{E_{l(>1)}} = 0 \quad (25. a), (25. b)$$

and those of deuterioethanes according to (17. a) and (24) as

$$V^{A_0} = y_0^2 \bar{v}(III), \quad V^{A_1} = 2y_0 y_1 \bar{v}(III), \quad V^{A_2} = y_1^2 \bar{v}(III), \quad V^{A_{n(>2)}} = 0. \quad (26)$$

Because of negligibly small $\gamma(H)^2$ compared with unity as seen from (16. a), we have by (14) and (4)

$$\bar{v}(I_b) = \bar{v}(III),$$

hence the relative evolution rates are given by (25) and (26) with reference to (19. a) as

$$V^{E_1} : V^{E_{l(>1)}} : V^{A_0} : V^{A_1} : V^{A_2} : V^{A_{n(>2)}} = 2(1 - y_1) : 0 : (1 - y_1)^2 : 2(1 - y_1)y_1 : y_1^2 : 0. \quad (27)$$

The relative rates depend thus solely on y_1 . We have from (21. H) neglecting X_1 by (22. a) and referring to (4),

$$\gamma(C_2H_5) \frac{\mathfrak{R}(II)}{\mathfrak{R}(I_b)} = \frac{3(1 - y_1)}{y_1}. \quad (28)$$

Eq.(14) gives on the other hand with neglect of $\gamma(H)^2$ compared with unity,

$$\gamma(H) - \gamma(C_2H_5) = \mathfrak{R}(I_b) / \mathfrak{R}(II), \quad \gamma(H)\gamma(C_2H_5) = \mathfrak{R}(I_b) / \mathfrak{R}(III).$$

Eliminating $\gamma(H)$ and $\gamma(C_2H_5)$ from the above three equations, we have

Theory of Hydrogenation of Ethylene on Metallic Catalyst IV

$$y_1 = \frac{3}{2} \cdot \frac{-5 + \sqrt{1 + 4\kappa}}{\kappa - 6}, \quad (29. y)$$

where

$$\kappa \equiv \mathfrak{R}(\text{II})^2 / \mathfrak{R}(\text{I}_b) \mathfrak{R}(\text{III}). \quad (29. \kappa)$$

Eq. (29. y) states that y_1 is the sole function of κ , which increases monotonously from zero to unity, as κ decreases from infinity to zero.

The κ is calculated by (29. κ) on the base of (7) with values of constants given by (8) and (9), hence y_1 and relative rates are worked out by (29. y) and (27) in percent of total evolution rates of deuterioethylenes and deuterioethanes as shown in Table I in comparison with the experimental results of KEMBALL at twenty percent completion of hydrogenation¹³⁾.

TABLE I. Evolution rates of deuterioethylenes and deuterioethanes in course of catalyzed deuteration of light ethylene in the presence of nickel catalyst. -100°C , $P^E = 2.7$ mmHg, $P^H = 8.1$ mmHg.

Quantities	κ	y_1	V^E_l				V^A_n						
			$l=1$	2	3	4	$n=0$	1	2	3	4	5	6
Theoretical Values*)	100.8 (187.7)	0.239 (0.185)	60.3 (62.0)	0 (0)	0 (0)	0 (0)	23.0 (25.2)	14.4 (11.5)	2.3 (1.3)	0 (0)	0 (0)	0 (0)	0 (0)
Experimental Values**)	—	—	46.7	13.2	2.7	0.7	7.8	12.5	9.5	4.0	2.0	0.8	0.2

*) Initial values.

***) Twenty percent hydrogenation completed.

Theoretical values in the parentheses are those of “accurate” calculation referred to in §2 without substitution of $T_N \exp\left(1 - \frac{T_N}{T}\right)$ for T . The theoretical results, either “approximate” or “accurate”, may be taken approximately concordant with the experimental result at twenty percent completion of hydrogenation, in consideration of the initial enhancement of E_1 theoretically predicted, which causes by accumulation up to twenty percent completion of hydrogenation to the subsequent increase of higher deuterioethylenes and deuterioethanes at the cost of lower ones. The “accurate” or “approximate” calculation could be preferred to the other neither in this regard nor theoretically as referred to in §2. We might rather draw a few experimentally verifiable conclusions from the “approximate” form of (7), both widely and so far confirmed by experiment with numerical values of (8) and (9) in the next section.

§ 6. Discussion

We have seen by (27) and (29. y) that the relative evolution rates are determined by a single variable κ , which depends on temperature and partial pressures. We have from (29. κ), (7) and (9) that

$$\kappa = \frac{Q_P^H}{P^H} \left(\frac{P^E}{Q_P^E} \right)^{0.475} \exp\left(-\frac{0.304 \text{ Kcal}}{RT}\right),$$

which shows that κ increases, although very slowly, with increase of temperature. The increase of temperature alone from -100 C to 90 C results in the increase of κ by 1.6 factor according to the above equation, which would give $y_1=0.194$ by (29. y). This result is numerically nearly valid^{*}), although the neglect of $r(\text{H})^2$, upon which (29. y) rests is no more exact, indicating qualitatively by (27) the predominance of light ethane in accordance with the experimental result of TURKEVICH *et al.*⁶⁾. It may be noted that further increase of temperature leads to that of dideuteroethane on the base of $\mathfrak{R}(s)$'s given by (7), (8) and (9) similarly as deduced by KEM¹²⁾ in terms of previous expressions of $\mathfrak{R}(s)$'s.

We see from the above equation on the other hand that κ varies appreciably with partial pressures. By increasing for instance P^H fiftyfold or decreasing it to one tenth at the experimental condition of KEMBALL we have $\kappa = 2.02$ or $\kappa = 1008$, from which the evolution rates are calculated by (29. y) and (27) as shown respectively in the second and third rows of the Table below.

TABLE II. Evolution rates of deuteroethylenes and deuteroethanes in course of catalyzed deuteration of light ethylene in the presence of nickel catalyst (theoretical) -100°C , $P^E = 2.7$ mmHg.

P^H mmHg	y_1	V^{E_1}	$V^{E_{l(>1)}}$	V^{A_0}	V^{A_1}	V^{A_2}	$V^{A_{n(>2)}}$
405	0.750	33.3	0	4.2	25.0	37.5	0
0.81	0.088	64.4	0	29.4	5.7	0.3	0

At higher P^H the initial evolution rate of E_1 is thus relatively low and that of A_n increases with increase of n from 0 to 2, abruptly vanishing as n exceeds 2, while at lower P^H , V^{E_1} is appreciably high and V^{A_n} decreases with increase of n from 0 to 2 and vanishes for n greater than 2. This would illustrate a versatile dependence of the distribution of deuterocompounds on the experimental conditions on the basis of the associative mechanism.

^{*}) We have $r(\text{H})=0.706$ and $r(\text{C}_2\text{H}_5)=0.668$ by solving (14) for them at 90°C , $P^E=2.7$ mmHg and $P^H=8.1$ mmHg on the base of (7), (8), and (9), which give $y_1=0.256$ instead by (28).

Summary

HORIUTI's method^{1,3)} of deriving the rates of reactions associated with the catalyzed hydrogenation from the associative mechanism in terms of the statistical-mechanical functions $\mathfrak{K}(s)$'s each relevant to the constituent step s of the mechanism was applied to accounting for the experimental result of KEMBALL¹³⁾ on the catalyzed deuteration of light ethylene in the presence of nickel catalyst at -100°C , that light, monodeutero- and dideuteroethanes were most abundant among the deuteration products with a peak at monodeuteroethane, being accompanied by several times rapid an evolution of monodeuteroethylene.

Using $\mathfrak{K}(s)$ recently revised by HORIUTI allowing for the effect of adsorption⁴⁾ the above experimental results were satisfactorily accounted for. It was shown on the same basis that the relative abundance of deutoethylenes and deuterioethanes varies variously with partial pressures of reactants.

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