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## MECHANISTIC ANALYSIS OF STEADY HETEROGENEOUS CATALYSIS

### Application to Hydrogenolysis of Cyclopentanone over Tungsten Catalyst

By

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#### Abstract

The general method previously developed for the mechanistic analysis of the steady rates of chemical reactions was applied to the hydrogenolysis of cyclopentanone catalyzed by tungsten, a prototype of a complex heterogeneous catalysis. It was concluded that at an early stage of the reaction equilibrium is established for the formation of cyclopentanol from cyclopentanone assumed to be caused by three steps, *i.e.*, the steps of adsorption of hydrogen (a) and cyclopentanone (b) and the surface combination (c) of cyclopentanone with hydrogen adatoms into cyclopentanol, and the last one is the slowest among them. The step (d) of formation of half-hydrogenated complex of cyclopentene and that (e) of desorption of water vapor were supposed to be practically in equilibrium, and, further, the step (f) of fission of carbon-oxygen bond and that (g) of formation of cyclopentane from the half-hydrogenated complex of cyclopentene were concluded to be practically irreversible.

The heats of activation, 10.1 and 4.8 kcal/mole, observed for formation of cyclopentene and cyclopentane were attributed, respectively, to step (g), mentioned above, and that (h) of cyclopentane formation from the half-hydrogenated complex of cyclopentene and adsorbed hydrogen. The retardation effect of  $C_5$  hydrocarbons and  $H_2O$  on hydrogenation of cyclopentene were found to be negligible as compared with that of ketone and/or alcohol.

The results at the early stage of the hydrogenolysis were extrapolated to its later stage in conformity with the experimental results that hydrogenation of cyclopentene appeared to be accelerated when ketone and alcohol are completely consumed, where the rate-determining step of the hydrogenation was concluded to switch from step (g) to (a).

#### Introduction

In the previous paper<sup>1)</sup> a general method of estimation of the rates of constituent steps and the fugacities of intermediates of a chemical

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reaction in its steady state has been developed without the use of the kinetic mass-action law currently assumed with respect to individual steps. In the present paper the validity of the method is investigated by applying it to more complicated, heterogeneous catalysis, *i.e.*, the hydrogenolysis of cyclopentanone catalyzed by tungsten film, which has been observed by KEMBALL and STODDART<sup>2)</sup> to produce cyclopentanol, cyclopentene, cyclopentane and water even at an early stage of the reaction between 1.19 mmHg cyclopentanone and 17.85 mmHg hydrogen at 136°C.

KEMBALL and STODDART<sup>2)</sup> have observed the time courses of respective components\*) as well as the deuterium distribution in cyclopentanone in the case of hydrogenolysis with deuterium and derived some qualitative conclusions as follows. a) Cyclopentanone and cyclopentanol are in equilibrium after a few minutes from the start of the reaction, as seen from the observed result that the formation of alcohol was instantaneously completed at the very initial stage and it was consumed together with the ketone in the course of the hydrogenolysis. b) The dissociation of the secondary carbon-metal bond of the half-hydrogenated complex of ketone may be slow as suggested by the kinetics of the hydrogenolysis similar to that of hydrogenation of acetone<sup>3)</sup>. c) The ketone and alcohol inhibit the hydrogenation of cyclopentene to cyclopentane.

Referring to the above conclusions, a set of probable steps was assumed in the present work and their rates and the fugacities of adsorbed intermediates were individually calculated under the steady state condition of this set of steps. The kinetic behaviour of the hydrogenolysis was then discussed with regard to its full course on the basis of the results of the analysis.

#### Methods and Results

##### 1. The set of steps and the sort of overall reactions to be caused simultaneously and linearly independent of each other.

Five adsorbed intermediates are assumed as follows.

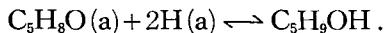
Taking into account the reaction being catalyzed by tungsten at a temperature above 100°C and the predominant evolution of monodeutero-cyclopentanone by deuteration of light cyclopentanone, we assume first the chemisorption of hydrogen to form adsorbed hydrogen adatoms, H(a)'s<sup>4)</sup>, and second an adsorbed complex of cyclopentanone, C<sub>5</sub>H<sub>8</sub>O(a).

Monodeutero-cyclopentanone can be formed by the forward and backward acts of the reaction,

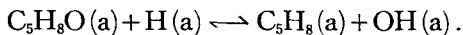
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\*) Cf. Ref. 2, Figure 4.

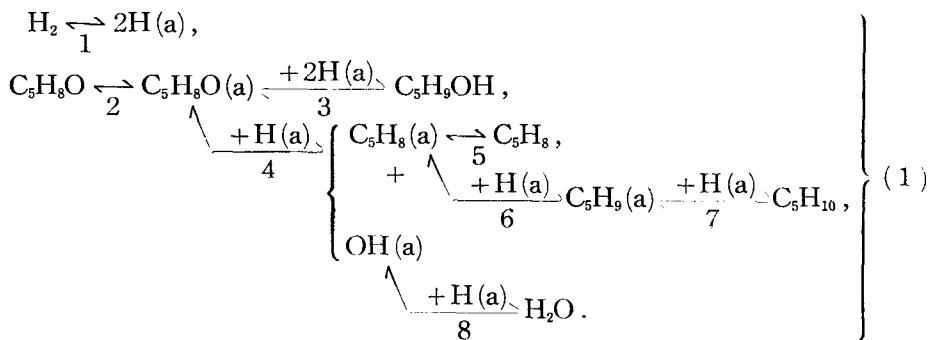
### *Steady Hydrogenolysis of Cyclopentanone on W*



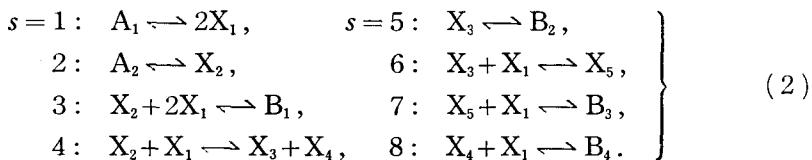
This reaction may be divided further into several steps as suggested by KEMBALL and STODDART<sup>2)</sup>, however, we treat it for the present as a single step to investigate the rough framework of the kinetic behaviour of the hydrogenolysis. Referring to the formation of cyclopentene and cyclopentane even at the initial stage of the reaction, we can probably assume the presence of adsorbed cyclopentene,  $C_5H_8(a)$ , and its half-hydrogenated complex,  $C_5H_9(a)$ , similarly to the case of the hydrogenation of mono-olefines<sup>5)</sup>. Finally, adsorbed OH radicals may be formed by the hydrogenative fission of carbon-oxygen bond of  $C_5H_8O(a)$  as



The following scheme of reaction is constructed as the simplest set of steps involving five intermediates assumed above.



Denoting the reactants,  $H_2$  and  $C_5H_8O$ , by  $A_1$  and  $A_2$ , products,  $C_5H_9OH$ ,  $C_5H_8$ ,  $C_5H_{10}$  and  $H_2O$ , by  $B_1$ ,  $B_2$ ,  $B_3$  and  $B_4$  and adsorbed intermediates,  $H(a)$ ,  $C_5H_8O(a)$ ,  $C_5H_8(a)$ ,  $C_5H_9(a)$  and  $OH(a)$ , by  $X_1$ ,  $X_2$ ,  $X_3$ ,  $X_4$  and  $X_5$ , respectively, scheme (1) is symbolized by the following set of eight steps:



The steady state condition of this set of steps is now given as

$$\left\{ d[X_i]/dt \right\} = (a_{is}) \left\{ v_s \right\} = 0 , \quad (3.v)$$

where  $\{d[X_i]/dt\}$  and  $\{v_s\}$  are the column matrices of  $i$  and  $s$  elements, respectively;  $[X_i]$  is the concentration of  $i$ -th intermediate,  $X_i$ , and  $v_s$  the

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net rate, *i.e.*, the number of the net, forward acts of  $s$ -th step in an unit time of reaction, respectively. The  $(a_{ts})$  is a matrix with five rows and eight columns and given as

$$(a_{ts}) = \begin{pmatrix} 2 & 0 & -2 & 1 & 0 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \end{pmatrix} \quad (3. a)$$

The rank,  $q$ , of  $(a_{ts})$  is five, hence we have  $s-q^6$ , *i.e.*, three, particular solutions,  $\{\nu_s\}_p$  ( $p=1, 2$  and  $3$ ), of equation (3. v) with respect to  $\{v_s\}$ , which are now chosen as

$$\left. \begin{array}{l} \{\nu_s\}_1 = \{1, 0, 0, 0, -1, 1, 1, 0\}, \\ \{\nu_s\}_2 = \{1, 1, 1, 0, 0, 0, 0, 0\}, \\ \{\nu_s\}_3 = \{0, 0, -1, 1, 1, 0, 0, 1\}. \end{array} \right\} \quad (3. v)$$

The general solution of equation (3. v) is then given as

$$\{v_s\} = \alpha \{\nu_s\}_1 + \beta \{\nu_s\}_2 + \gamma \{\nu_s\}_3 = \begin{pmatrix} \alpha + \beta \\ \beta \\ \beta - \gamma \\ \gamma \\ \gamma - \alpha \\ \alpha \\ \alpha \\ \gamma \end{pmatrix}, \quad (4. v)$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are the steady rates of three, linearly independent overall reactions, which are given by summing up steps (2), each multiplied by  $\nu_s$  of equation (3. v), as

$$\left. \begin{array}{ll} A_1 + B_2 = B_3 & (H_2 + C_5H_8 = C_5H_{10}), \\ A_1 + A_2 = B_1 & (H_2 + C_5H_8O = C_5H_9OH), \\ B_1 = B_2 + B_4 & (C_5H_9OH = C_5H_8 + H_2O), \end{array} \right\} \quad (4. R)$$

respectively. The particular solutions (3. v) or these three overall reactions linearly independent of each other are chosen to fit in with the observed results. The first one of (4. R) is the sole reaction observed in the later stage, the second is one nearly completed at the early stage of the hydrogenolysis, as observed by KEMBALL and STODDART<sup>2)</sup>, and the last one the

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simplest one linearly independent of the above two.

## 2. Rate-equations in the steady state

According to our method of analysis<sup>1)</sup> of the steady rate, we now define the particular values of the unidirectional rates of respective steps (2) as follows<sup>5,6)</sup>.

$$\left. \begin{array}{ll} u_1 \equiv (kT/h) a_{A_1} / a^{\pm(1)}, & u_2 \equiv (kT/h) a_{A_2} / a^{\pm(2)}, \\ u_3 \equiv (kT/h) a_{A_1} a_{A_2} / a^{\pm(3)}, & u_4 \equiv (kT/h) a_{A_1}^{1/2} a_{A_1} / a^{\pm(4)}, \\ u_5 \equiv (kT/h) a_{B_2} / a^{\pm(5)}, & u_6 \equiv (kT/h) a_{A_1}^{1/2} a_{B_2} / a^{\pm(6)}, \\ u_7 \equiv (kT/h) a_{A_1} a_{B_2} / a^{\pm(7)}, & u_8 \equiv (kT/h) a_{A_1} a_{A_2} / a_{B_2} a^{\pm(8)}, \end{array} \right\} \quad (5. u)$$

where  $k$ ,  $T$  and  $h$  have their usual meanings and  $a_{A_i}$  etc. or  $a^{\pm(1)}$  etc. are the absolute activities<sup>7)</sup> of the gaseous species,  $A_i$  etc., and of the critical complexes,  $\pm(1)$  etc., of steps, 1 etc., respectively. By the use of above  $u$ 's and referring to equation (4. v), the net rates,  $v_i$  etc., of respective steps are now given as

$$\left. \begin{array}{l} v_1 (=v_{1+}-v_{1-}) = u_1(1-f_1^2) = \alpha + \beta, \\ v_2 = u_2(1-f_2) = \beta, \\ v_3 = u_3(f_1^2 f_2 - F_\beta) = \beta - \gamma, \\ v_4 = v_8 = u_4(f_1 f_2 - f_3 f_4) = u_8(f_1 f_4 - F_\beta F_\gamma) = \gamma, \\ v_5 = u_5(f_3 - 1) = \gamma - \alpha, \\ v_6 = v_7 = u_6(f_1 f_3 - f_5) = u_7(f_1 f_5 - F_\alpha) = \alpha, \end{array} \right\} \quad (5. v)$$

where

$$\left. \begin{array}{ll} f_1 \equiv a_{A_1}^{X_1} / a_{A_1}^{1/2}, & f_2 \equiv a_{A_2}^{X_2} / a_{A_2}, \\ f_4 \equiv a_{A_1}^{X_4} a_{B_2} / a_{A_1}^{1/2} a_{A_2}, & f_5 \equiv a_{A_1}^{X_5} / a_{A_1}^{1/2} a_{B_2}, \end{array} \right\} \quad (5. f)$$

is the fugacity of  $X_i$  ( $i=1, 2, \dots$  or 5), i.e., the absolute activity of  $X_i$  referred to that of a set,  $(X_i)_{eq}$ , of reactants and/or products, from which  $X_i$  is formed by the acts of appropriate steps of scheme (2), and

$$\left. \begin{array}{ll} F_\alpha \equiv a_{B_2} / a_{A_1} a_{B_2}, \\ F_\beta \equiv a_{B_1} / a_{A_1} a_{A_2}, \\ F_\gamma \equiv a_{B_2} a_{B_4} / a_{B_1}, \end{array} \right\} \quad (5. F)$$

respectively. Taking account of that the absolute activity,  $a$ , relates to the chemical potential,  $\mu$ , as

$$kT \ln a = \mu,$$

we see that  $kT \ln f_i$  is the chemical potential of  $X_i$  referred to that of

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 $(X_i)_{eq}$ ; for instance,

$$kT \ln f_4 = \mu^{x_1} - (\mu_{A_1}/2 + \mu_{A_2} - \mu_{B_2}),$$

where  $(X_4)_{eq} = A_1/2 + A_2 - B_2$ . The logarithmic ratio of two terms in the parenthesis of the expression (5. v) of  $v_s$ , multiplied by  $kT$ , gives, thus, the difference between chemical potentials of the initial and the final systems, i.e., the free energy drop,  $\Delta G_s$ , of step  $s$ . With respect to step 4, for instance, we have

$$kT \ln (f_1 f_2 - f_3 f_4) = (\mu^{x_1} + \mu^{x_2}) - (\mu^{x_3} + \mu^{x_4}) = \Delta G_4.$$

The rate-equations with respect to three overall reactions (4. R) are now derived from equation (5. v) by eliminating all of  $f$ 's as follows.

$$\left. \begin{aligned} 1 - F_\alpha &= \frac{\alpha + \beta}{u_1} \left( 1 + \frac{\gamma - \alpha}{u_5} \right) + \frac{\alpha}{u_6} \left( 1 - \frac{\alpha + \beta}{u_1} \right)^{1/2} + \frac{\alpha}{u_7} + \frac{\gamma - \alpha}{u_5}, \\ 1 - F_\beta &= \frac{\alpha + \beta}{u_1} + \frac{\beta}{u_2} \left( 1 - \frac{\alpha + \beta}{u_1} \right) + \frac{\beta - \gamma}{u_3}, \\ F_\gamma (1 - F_\gamma) &= \frac{\beta - \gamma}{u_3} + \frac{\gamma}{u_4} \left( 1 - \frac{\alpha + \beta}{u_1} \right)^{1/2} + \frac{\gamma - \alpha}{u_5} F_\beta F_\gamma + \frac{\gamma}{u_8} \left( 1 + \frac{\gamma - \alpha}{u_5} \right). \end{aligned} \right\} (6)$$

### 3. Calculation of the values of $u$ 's and $f$ 's

The absolute activities,  $a_{A_1}$  etc., of gaseous components are proportional to their partial pressures,  $P_{A_1}$  etc., i.e.,

$$a_{A_1} = P_{A_1} U_{A_1}$$

etc., respectively, on the basis of the ideal gas approximation. The  $u$ 's of equation (5. u) are now rewritten, on the one hand, in the form of

$$\left. \begin{aligned} u_1 &= P_{A_1} U_1, & u_2 &= P_{A_2} U_2, & u_3 &= P_{A_1} P_{A_2} U_3, \\ u_4 &= P_{A_1}^{1/2} P_{A_2} U_4, & u_5 &= P_{B_2} U_5, & u_6 &= P_{A_1}^{1/2} P_{B_2} U_6, \\ u_7 &= P_{A_1} P_{B_2} U_7, & u_8 &= (P_{A_1} P_{A_2} / P_{B_2}) U_8, \end{aligned} \right\} (7. u)$$

where

$$\left. \begin{aligned} U_1 &\equiv (kT/h) U_{A_1} / a^{\pm(1)}, & U_2 &\equiv (kT/h) U_{A_2} / a^{\pm(2)}, \\ U_3 &\equiv (kT/h) U_{A_1} U_{A_2} / a^{\pm(3)}, & U_4 &\equiv (kT/h) U_{A_1}^{1/2} U_{A_2} / a^{\pm(4)}, \\ U_5 &\equiv (kT/h) U_{B_2} / a^{\pm(5)}, & U_6 &\equiv (kT/h) U_{A_1}^{1/2} U_{B_2} / a^{\pm(6)}, \\ U_7 &\equiv (kT/h) U_{A_1} U_{B_2} / a^{\pm(7)}, & U_8 &\equiv (kT/h) U_{A_1} U_{A_2} / U_{B_2} a^{\pm(8)}, \end{aligned} \right\} (7. U)$$

and they are nearly constant at a constant reaction temperature so far as the progress of the hydrogenolysis is as little as  $a^{\pm(1)}$  etc. remain unchanged.

The  $F_\alpha$ ,  $F_\beta$  and  $F_\gamma$  given by equations (5. F) are, on the other hand,

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expressed as

$$\left. \begin{array}{l} F_\alpha = (P_{B_3}/P_{A_1}P_{B_2})/K_\alpha, \\ F_\beta = (P_{B_1}/P_{A_1}P_{A_2})/K_\beta, \\ F_\gamma = (P_{B_2}P_{B_4}/P_{B_1})/K_\gamma, \end{array} \right\} \quad (7. F)$$

where  $K_\alpha$ ,  $K_\beta$  and  $K_\gamma$  are the equilibrium constants of reactions (4. R). Every  $F$ 's are thus observable.

Introducing the above expressions (7. u) of  $u$ 's into equations (6), we have the final form of the rate-equations for evaluation of  $u$ 's and  $f$ 's as follows.

$$1 - F_\beta + \beta x_1 x_2 = P_{A_2} x_1 + P_{A_1} \beta x_2 / (\alpha + \beta) + (\beta - \gamma) x_3 / (\alpha + \beta), \quad (8. 1. x)$$

$$f_1 = (1 - (\alpha + \beta) x_1 / P_{A_1})^{1/2}, \quad f_2 = 1 - \beta x_2 / P_{A_2}, \quad (8. 1. f)$$

$$\left. \begin{array}{l} P_{B_2} (1 - F_\alpha - (\alpha + \beta) / u_1) = (\gamma - \alpha) (1 + (\alpha + \beta) / u_1) x_5 \\ \quad + (\alpha f_1 / P_{A_1}^{1/2}) x_6 + \alpha x_7 / P_{A_1}, \end{array} \right\} \quad (8. 2. x)$$

$$f_3 = 1 + (\gamma - \alpha) x_5 / P_{B_2}, \quad f_5 = (\alpha / u_7 + F_\alpha) / f_1, \quad (8. 2. f)$$

$$\left. \begin{array}{l} P_{A_1} P_{A_2} F_\beta (1 - F_\gamma) - (\beta - \gamma) x_3 - (\gamma - \alpha) P_{A_1} P_{A_2} F_\beta F_\gamma / u_5 \\ \quad = P_{A_1}^{1/2} \gamma f_1 x_4 + \gamma P_{B_2} f_3 x_8, \end{array} \right\} \quad (8. 3. x)$$

$$f_4 = (f_1 f_2 - \gamma / u_4) / f_3, \quad (8. 3. f)$$

where

$$x_s \equiv 1/U_s, \quad (s = 1, 2, \dots, 8). \quad (8. 4)$$

We see from equations (8) that  $x$ 's, accordingly  $u$ 's and  $f$ 's, can be evaluated on the basis of three sets of values of partial pressures,  $P_{A_1}$  etc., and the steady rates,  $\alpha$  etc., in a narrow range of the course of hydrogenolysis. In the present calculation those values at 15, 20, 25 and 30 min of reaction time are used for the analysis of the early stage of the reaction. The plots of  $C_5\%$  given by KEMBALL and STODDART<sup>2)</sup> during the early 50 min are replaced by smoothed curves and their values at these four times of reaction are multiplied by  $1.19 \times 10^{-2}$  mmHg to obtain the partial pressures,  $P_{A_2}$ ,  $P_{B_1}$ ,  $P_{B_2}$  and  $P_{B_3}$ , which are given in Table 1. The partial pressures,  $P_{B_4}$  and  $P_{A_1}$ , are evaluated by taking into account the mass balances,

$$P_{B_4} = P_{B_2} + P_{B_3}$$

and

$$P_{A_1} = 17.85 - (P_{B_1} + P_{B_2} + P_{B_3}) \text{ mmHg.}$$

As seen from reactions (4. R), their steady rates,  $\alpha$ ,  $\beta$  and  $\gamma$ , are given as

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TABLE 1. Partial pressures (in mmHg) of gaseous components of the reaction between 1.19 mmHg cyclopentanone and 17.85 mmHg hydrogen over tungsten film at 136°C<sup>2</sup>.

time min	cyclo- pentanone (A <sub>1</sub> )	cyclo- pentanol (B <sub>1</sub> )	cyclo- pentene (B <sub>2</sub> )	cyclo- pentane (B <sub>3</sub> )	water (B <sub>4</sub> )	hydrogen (A <sub>1</sub> )
15	0.574	0.105	0.344	0.193		
20	0.514	0.097	0.396	0.205	0.603	17.153
25	0.458	0.089	0.448	0.214	0.662	17.100
30	0.405	0.071	0.497	0.223	0.720	17.059

TABLE 2. The steady rates and the values of *F*'s of three overall reactions (4. R).

time min	$\alpha$	$\beta$ mmHg/min	$\gamma$	$F_\alpha$	$F_\beta$	$F_\gamma$
20	0.0108	0.0120	0.0131	$1.91915 \times 10^{-8}$	1.0	$1.54229 \times 10^{-3}$
25	0.0104	0.0113	0.0123	$1.78039 \times 10^{-8}$	1.0	$2.09279 \times 10^{-3}$
30	0.0099	0.0105	0.0116	$1.67210 \times 10^{-8}$	1.0	$3.15801 \times 10^{-3}$

$$\alpha = V_{B_3}, \quad \beta = -V_{A_2} \quad \text{and} \quad \gamma = V_{B_2} + V_{B_3}, \quad (8. V)$$

where  $V_{B_3}$ , etc. are the increasing rates of  $P_{B_3}$ , etc., respectively, which are estimated, as given in Table 2, from each increments of  $P_{B_3}$ , etc. during five minutes just before the specified time of reaction.

The values of  $K_\alpha$  and  $K_\gamma$  in equations (7. F) at 136°C are evaluated from the free energies of formation of respective components of the first and third ones of reactions (4. R)<sup>8</sup> as

$$K_\alpha = 1.57305 \times 10^6 \text{ mmHg}^{-1}, \quad K_\gamma = 1.5870 \times 10^3 \text{ mmHg}, \quad (8. K)$$

respectively. There is no data available for evaluation of  $K_\beta$ . Provided that  $K_\beta$  is close to the equilibrium constant of the hydrogenation of cyclohexanone to cyclohexanol<sup>9</sup>, we have

$$K_\beta = 1.112 \times 10^{-2} \text{ mmHg}^{-1},$$

which is close to the value,

$$P_{B_1}/P_{A_1} P_{A_2} = 1.06 \times 10^{-2} \text{ mmHg}^{-1},$$

estimated from the date of Table 1 at  $t=20, 25$  or  $30$  min, and, thus,  $F_\beta$  is approximated by unity, which means the equilibrium of the second reac-

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tion of (4. R) as suggested by KEMBALL and STODDART<sup>2)</sup>. The value of  $F_\alpha$ ,  $F_\beta$  and  $F_\gamma$  evaluated according to equations (7. F) and (8. K) are given in Table 2.

Introducing the three sets of values of  $\alpha$ ,  $\beta$ ,  $P_{A_1}$  and  $P_{A_2}$  at  $t=20$ , 25 and 30 min from Tables 1 and 2 into equation (8. 1. x), we have

$$\left. \begin{array}{l} x_1 \equiv 1/U_1 = 6.87 \times 10^{-4}, \\ x_2 \equiv 1/U_2 = 3.91 \times 10^{-5}, \\ x_3 \equiv 1/U_3 = 1.24 \times 10^{-2}, \end{array} \right\} \quad (9. x)$$

and further from equations (8. 1. f)

$$f_1 = 0.99999956, \quad f_2 = 0.99999898 \quad (9. f)$$

at  $t=25$  min, respectively. These values of  $f$ 's are nearly constant with a little progress of the reaction; e.g.,  $f_1$  is 0.99999954 at  $t=20$  min and 0.99999959 at 30 min.

The values of  $x_5$ ,  $x_6$ ,  $x_7$ ,  $f_3$  and  $f_5$  are now evaluated by equations (8. 2. x) and (8. 2. f), referring to the first one of equations (7. 1) and (9. x), as

$$\left. \begin{array}{l} x_5 \equiv 1/U_5 = 2.06 \times 10^2, \\ x_6 \equiv 1/U_6 = -8.73 \times 10^2, \\ x_7 \equiv 1/U_7 = 5.00 \times 10^3, \end{array} \right\} \quad (10. x)$$

and

$$f_3 = 1.876, \quad f_5 = 6.791 \quad (\text{at } t=25 \text{ min}), \quad (10. f)$$

respectively. All  $x$ 's should not be negative according to the definition of  $U$  and, thus the negative value evaluated for  $x_6$  suggests some error of the observed date given in Table 1 or the unreality of scheme (1). Provided that the negative  $x_6$  arises from an error of observation, we now introduce a rule of crude approximation that the real value of apparently negative  $x$  is considered to be nearly zero. There is some support of this approximation with respect to  $x_6$  as discussed later. Assuming  $x_6 \approx 0$ , we have from equation (8. 2. x) and the experimental data of Table 1 at  $t=20$  and 25 min that

$$x_5 = 2.03 \times 10^2, \quad x_7 = 1.37 \times 10^3 \quad (x_6 \approx 0), \quad (11. x)$$

which are not far different from those given by equations (10. x). It follows from equations (8. 2. f) that

$$f_3 = f_5 = 1.864 \quad (\text{at } t=25 \text{ min}), \quad (11. f)$$

from which we have  $f_1 f_3 - f_5 \approx 0$  due to  $f_1 \approx 1$ . This relation among  $f_1$ ,  $f_3$

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and  $f_5$  shows the equilibrium of step 6 consisting with the approximation of  $x_6 \approx 0$  or  $u_6 \approx \infty$ .

Finally, it follows from equation (8. 3. x) by introducing into it the data at  $t=20$  and 25 min that

$$x_4 = 1.83 \times 10^2 \quad \text{and} \quad x_8 = -1.26 \times 10^2.$$

Applying again the rule of approximation to  $x_8$ , we have from equation (8. 3. x) that

$$x_4 \equiv 1/U_4 = 9.70 \times 10^2 \quad (x_8 \equiv 1/U_8 \approx 0), \quad (12. x)$$

which is not far different from the above value of  $x_4$ . Further, from the relation,  $f_1 f_4 - F_\beta F_r \approx 0$ , derived from  $\gamma = u_8 (f_1 f_4 - F_\beta F_r)$  by taking account of  $\gamma \neq 0$  and  $u_8 \approx \infty$ , it follows that

$$f_4 \approx F_r = 2.093 \times 10^{-3} \quad (t=25 \text{ min}). \quad (12. f)$$

A negative value is derived for  $f_4$  from the relation,  $\gamma = u_4 (f_1 f_2 - f_3 f_4)$ , and the value of  $f_3$  of equations (11. f), and shows that the above estimation of  $x_4$  by assuming  $x_8 \approx 0$  is somewhat excessive.

The values of  $U$ 's and  $u$ 's at 25 min derived from those of  $x$ 's according to equations (7. u) are given in Table 3 together with those of  $f$ 's.

TABLE 3. Values of  $U$ 's and  $u$ 's of respective steps and those of  $f$ 's of respective intermediates at  $t=25$  min.

$U_1$	$1.4536 \times 10^3$	$u_1$	$2.4860 \times 10^4$	$f_1$	0.99999956
$U_2$	$2.5606 \times 10^4$	$u_2$	$1.1710 \times 10^4$	$f_2$	0.99999898
$U_3$	8.0744	$u_3$	$6.3164 \times 10^2$	$f_3$	1.864
$U_4$	$1.0308 \times 10^{-3}$	$u_4$	$1.9502 \times 10^{-3}$	$f_4$	$2.093 \times 10^{-3}$
$U_5$	$4.9169 \times 10^{-3}$	$u_5$	$2.1200 \times 10^{-3}$	$f_5$	1.864
$U_6$	$\infty$	$u_6$	$\infty$		
$U_7$	$7.2930 \times 10^{-4}$	$u_7$	$5.5805 \times 10^{-3}$		
$U_8$	$\infty$	$u_8$	$\infty$		

### Discussion

There remains some ambiguity in the present results of calculation with respect to steps 6 and 8,  $x$ 's of which were apparently negative and supposed to be nearly zero. The crude approximation of  $x_6 \approx 0$  is in conformity with the conclusion on catalytic hydrogenation of monoolefines<sup>5)</sup> over metals that the step of adsorbed olefine to form its half-hydrogenated complex is in quasi-equilibrium. In spite of such a crude approximation of

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in the present analysis, the kinetic behaviour of the hydrogenolysis can be consistently discussed as follows.

As discussed in the previous paper<sup>1)</sup> the values of  $u$ 's are the upper limits of the unidirectional rates of respective steps under the specified experimental condition and the smallest one among  $u$ 's of steps consisting of any one of overall reactions (4. R) gives the upper limit of the steady rate,  $\alpha$ ,  $\beta$  or  $\gamma$ , of the overall reaction. The value of  $f_i$  gives the chemical potential of the intermediate,  $X_i$ , referred to the set,  $(X_i)_{eq}$ , of appropriate gas components from which  $X_i$  is formed, as shown in foregoing Methods and Results.

According to the results of Table 3 we see the relative magnitudes of  $u$ 's are

$$u_6, u_8 \gg u_1 > u_2 > u_3 \gg u_7 > u_5 \cong u_4.$$

Three overall reactions (4. R) consist of sets of steps (1, 5, 6, 7), (1, 2, 3) and (3, 4, 5, 8), respectively, as seen from the particular solutions (3.  $\nu$ ) of the steady state condition (3.  $\nu$ ). The second overall reaction consisting of relatively fast steps, 1, 2 and 3, should attain its equilibrium much faster than the other two, in conformity with the value of  $F_\beta$  estimated as unity. The establishment of equilibrium of individual steps, 1, 2 and 3, is also informed by the remarkably large values of  $u$ 's of these steps. The values of  $f_1$  and  $f_2$  estimated as very close to unity directly show the equilibrium of steps 1 and 2, on account of  $1-f_1^2 \cong 0$  and  $1-f_2 \cong 0$ , i.e.,  $\Delta G_1 \cong 0$  and  $\Delta G_2 \cong 0$ , respectively. They give further that

$$f_1^2 f_2 - F_\beta \cong 0,$$

which is synonymous with the equilibrium of step 3. The smallest value of  $u_3$  among  $u$ 's of these three steps support the conclusion b) of KEMBALL and STODDART<sup>2)</sup> mentioned in Introduction.

The equal values of  $f_3$  and  $f_5$  as well as the approximation,  $x_6 \cong 0$ , i.e.,  $u_6 \cong \infty$ , means the equilibrium of step 6.

The value of  $f_3$  estimated as close to unity shows a small free energy drop of step 5, however, it is not in equilibrium on account of a small value of  $u_5$ . In contrast with step 5, the free energy drop of step 7 is far large because of  $f_1 f_5 / F_\alpha = 1.05 \times 10^8 \gg 1$ . It is, thus, concluded, taking into account the value of  $u_7$  as small as  $u_5$ , that step 7 is practically irreversible at the early stage of the hydrogenolysis. The relative rates of formation of cyclopentene and cyclopentane at this stage depend thus practically upon the relative magnitudes of  $u_5$  and  $u_7$ , and the activation energies, 10.1 and 4.8 kcal/mole, observed by KEMBALL and STODDART<sup>2)</sup> for the formation of

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cyclopentene and cyclopentane are practically attributed to steps 5 and 7, hence to the temperature coefficients of  $U_5$  and  $U_7$ , respectively.

As seen from equations (5. v), we have

$$v_4 = u_4(f_1f_2 - f_3f_4) = v_5 + v_7.$$

The value of  $u_4$  is the smallest among  $u$ 's and, further, it follows from the results of Table 3 that

$$f_1f_2/f_3f_4 = 2.2 \times 10^2 \gg 1,$$

hence it is concluded that step 4 is practically irreversible and the activation energy of this step, *i.e.*, the temperature coefficient of  $U_4$ , can be determined as that of the sum of rates of formation of cyclopentene and cyclopentane, which is expected to have a value intermediate of 4.8 and 10.1 kcal/mole.

The value of  $v_5 = u_5(f_3 - 1)$  does not become negative so far as  $f_3 \geq 1$ ; this is just the retardation effect of ketone and alcohol on the hydrogenation of cyclopentene observed of KEMBALL and STODDART<sup>2)</sup>.

The values of  $U$ 's may vary with the progress of reaction due to the change of its factor,  $a^{\pm(s)}$ , caused by variation of the interaction of  $\mp(s)$  with its surrounding species, however, we can qualitatively discuss the profile of the reaction in its later stage on the basis of the relative magnitudes of  $U$ 's given in Table 3 as follows. Because of the comparatively small values of  $u_4$ ,  $u_5$  and  $u_7$  and extremely large drop of the free energy of step 7, as mentioned above, the third one of reactions (4. R) may attain its equilibrium much faster than the first one involving step 7. In such a case, we have  $F_7 \approx 1$ , hence  $f_4$  is close to unity on account of that  $r = v_8 = v_8(f_1f_4 - F_8F_7)$  is small and finite, whereas  $u_8 \approx \infty$ ,  $f_1 \approx 1$  and  $F_8 = 1$ . Ketone and alcohol must be completely consumed at the equilibrium of the second and the third reactions of (4. R), because the equilibrium constant,  $K_r$ , of the latter reaction is large enough as given by equation (8. K). The value of  $f_3$  decreases then close to unity on account of the equilibrium of the third reaction of (4. R), hence of  $v_4 = u_4(f_1f_2 - f_3f_4) \approx 0$ , where  $f_1 \approx 1$  and  $f_2 \approx 1$ . It is, thus, concluded that the first reaction, *i.e.*, the hydrogenation of cyclopentene, becomes to be accelerated when ketone and alcohol are consumed completely and, consequently,  $f_3$  decreases smaller than unity, making  $v_5$  negative, hence cyclopentene to be consumed to form cyclopentane through steps 5, 6 and 7.

At the later stage of the hydrogenolysis where the reaction observed was solely the first one of (4. R), we can qualitatively discuss the relative magnitudes of the rates of its constituent steps on the basis of the partial

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pressure dependence of the steady rate,  $\alpha$ , of this single overall reaction. It follows in this case from equations (5. v) and (7. U) that

$$1/\alpha = x_1/P_{A_1} + x_5 f_1^2/P_{B_2} + x_6 f_1/(P_{A_1}^{1/2} P_{B_2}) + x_7/(P_{A_1} P_{B_2}).$$

With reference to the experimental fact that the steady rate,  $\alpha = V_{B_2}$ , was constant independent of  $P_{A_1}$  and  $P_{B_2}$  at the later stage of the reaction where the fractional change of  $P_{B_2}$  was marked, but  $P_{A_1}$  remained nearly unchanged, the first term in the right hand-side of the above equation must be far larger than the other terms, which depend on  $P_{B_2}$ . We have, thus,

$$x_1 \gg x_5, x_6, x_7 \quad (\text{or } U_1 \ll U_5, U_6, U_7).$$

This result shows, comparing with those given in Table 3 of  $U$ 's at the early stage of the hydrogenolysis, that steps 5 and 7 are remarkably accelerated beyond step 1 at the later stage by consumption of ketone ( $A_1$ ) and alcohol ( $B_1$ ). It is now concluded that the backward act of step 5 (*i.e.*, the re-adsorption of cyclopentene ( $B_2$ ) formed) and the forward act of step 7 (*i.e.*, the formation of cyclopentane ( $B_3$ ) from half-hydrogenated complex,  $X_5$ , of  $B_2$ ) are strongly retarded by the existence of the adsorbed complex ( $X_2$ ) of ketone and/or alcohol. We see that the consumption of ketone and alcohol causes the switching of the rate-determining step of the hydrogenation of cyclopentene ( $B_2 + A_1 = B_3$ ) from step 7 at the earyl stage of the hydrogenolysis to step 1 at the later stage.

A little retardation effect of  $H_2O$  on formation of cyclopentanol may be concluded from the present result of  $u_4$   $u_1$ ,  $u_2$  and  $u_3$ , which shows that the amount or the chemical potential of  $H_2O$  hardly affects the reaction. The effect of  $H_2O$  on the hydrogenation of cyclopentene is similarly much smaller than that of ketone and/or alcohol, because of the observed acceleration of the former reaction in spite of the increase of  $H_2O$ .

KEMBALL and STODDART<sup>2)</sup> have attempted to interprete the retardation of the formation of  $C_5$  hydrocarbons ( $B_2$  and  $B_3$ ) at an early stage of the hydrogenolysis by the re-adsorption of  $C_5$  hydrocarbons produced. The formation rate of  $C_5$  hydrocarbons was, however, found experimentally<sup>2)</sup> to be nearly constant independent of the amount of  $C_5$  hydrocarbons and, further, concluded by the present analysis to be nearly equal to the forward unidirectional rate of step 4, which is given as

$$v_{4+} = P_{A_1}^{1/2} P_{A_2} U_4 f_1 f_2$$

independent of  $P_{B_2}$  and  $P_{B_3}$ . As  $P_{A_1}$ ,  $f_1$  and  $f_2$  remain nearly constant, the term,  $P_{A_2} U_4$ , has to be constant, hence  $U_4$  must be proportional to  $1/P_{A_2}$  in the course of the hydrogenolysis. This change of  $U_4$  may be understood

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as caused by the decrease of the repulsion of  $X_2$  upon the critical complex of step 4 in the course of reaction, where  $X_2$  is constantly equilibrated with decreasing  $A_2$ .

The value of  $f_i$  does not uniquely relate to the amount of  $X_i$  on the catalyst surface because of that the species adsorbed on the surface may generally not behave as an ideal solution, however, referring to the relatively small values of  $u_4$ ,  $u_5$  and  $u_7$  and the large free energy drops of steps 4 and 7, it may be concluded that the catalyst surface is covered mainly by  $X_2$  (adsorbed cyclopentanone and/or its half-hydrogenated complex as suggested by KEMBALL and STODDART<sup>2)</sup> and partly by adsorbed cyclopentene ( $X_3$ ) and its half-hydrogenated complex ( $X_5$ ) at the early stage of the hydrogenolysis.

It is additionally noted that each of adsorbed intermediates is assumed in the present analysis to have an unique value of its fugacity, that is, the catalyst surface is homogeneous for individual intermediates. However, the analysis is independent of whether the adsorbed species are competitive on the same sites on the surface or not. Such detailed, kinetic informations, inclusive of the availability of the kinetic mass-action law for steps including adsorbed species, can be obtained by the similar analysis of experimental data at different partial pressures and reaction temperatures as well as those of the amounts of adsorption during the hydrogenolysis. A part of such an analysis has been given in the previous paper<sup>1)</sup> with respect to the oxidation of ethylene catalyzed by silver.

In conclusion, the present method is shown to be considerably effective for the kinetic analysis of the steady rates of complex heterogeneous catalysis, provided that its constituent steps are proved by appropriate theories and/or experiments.

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