Title	MECHANISTIC ANALYSIS OF STEADY HETEROGENEOUS CATALYSIS : Application to Hydrogenolysis of Cyclopentanone over Tungsten Catalyst
Author(s)	MIYAHARA, Koshiro
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 20(2), 71-84
Issue Date	1972-08
Doc URL	https://hdl.handle.net/2115/24936
Type	departmental bulletin paper
File Information	20(2)_P71-84.pdf

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 20, No. 2, pp. 71 to 84 (1972)

MECHANISTIC ANALYSIS OF STEADY HETEROGENEOUS CATALYSIS

Application to Hydrogenolysis of Cyclopentanone over Tungsten Catalyst

By

Koshiro MIYAHARA*

(Received December 28, 1971)

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 nogligible 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[1] a general method of estimation of the rates of constituent steps and the fugacities of intermediates of a chemical

---

*) Research Institute for Catalysis, Hokkaido University, Sapporo, Japan

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[2)] 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[2)] 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 intial 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[3)]. 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[4)], and second an adsorbed complex of cyclopentanone, C_5H_8O(a).

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

---

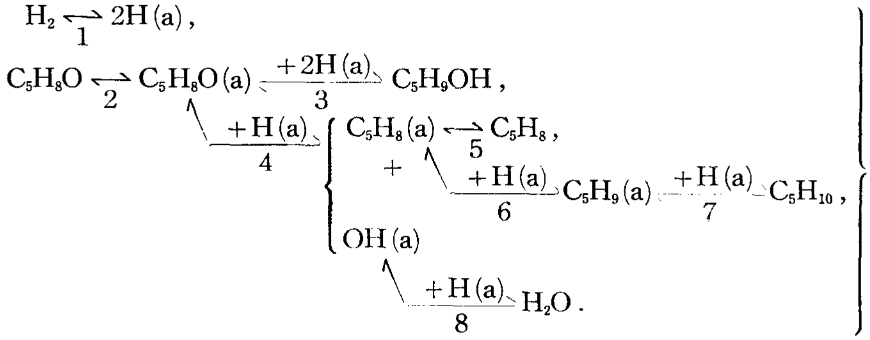
[*)] Cf. Ref. 2, Figure 4.

$$C_5H_8O\,(a) + 2H\,(a) \rightleftharpoons C_5H_9OH\,.$$

This reaction may be divided further into several steps as suggested by KEMBALL and STODDART[2], 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[5]. Finally, adsorbed OH radicals may be formed by the hydrogenative fission of carbon-oxygen bond of $C_5H_8O\,(a)$ as

$$C_5H_8O\,(a) + H\,(a) \rightleftharpoons C_5H_8\,(a) + OH\,(a)\,.$$

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



(1)

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 :

$$\left.\begin{array}{rlrl} s=1: & A_1 \rightleftharpoons 2X_1\,, & s=5: & X_3 \rightleftharpoons B_2\,, \\ 2: & A_2 \rightleftharpoons X_2\,, & 6: & X_3+X_1 \rightleftharpoons X_5\,, \\ 3: & X_2+2X_1 \rightleftharpoons B_1\,, & 7: & X_5+X_1 \rightleftharpoons B_3\,, \\ 4: & X_2+X_1 \rightleftharpoons X_3+X_4\,, & 8: & X_4+X_1 \rightleftharpoons B_4\,. \end{array}\right\} \qquad (2)$$

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

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

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

$$(a_{is}) = \begin{pmatrix} 2 & 0 & -2 & 1 & 0 & -1 & -1 & -1 \\ 0 & 1 & -1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \end{pmatrix}. \qquad (3.\,a)$$

The rank, q, of (a_{is}) 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

$$\left.\begin{aligned} \{\nu_s\}_1 &= \{1,\ 0,\ 0,\ 0,\ -1,\ 1,\ 1,\ 0\}\,, \\ \{\nu_s\}_2 &= \{1,\ 1,\ 1,\ 0,\ 0,\ 0,\ 0,\ 0\}\,, \\ \{\nu_s\}_3 &= \{0,\ 0,\ -1,\ 1,\ 1,\ 0,\ 0,\ 1\}\,. \end{aligned}\right\} \qquad (3.\,\nu)$$

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

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

where α, β and γ are the steady rates of three, linearly independent overall reactions, which are given by summing up steps (2), each multiplied by ν_s of equation (3. ν), as

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

respectively. The particular solutions (3. ν) 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[2], and the last one the simplest one linearly independent of the above two.

2. Rate-equations in the steady state

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

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

where k, T and h have their usual meanings and a_{A_1} *etc.* or $a^{\ddagger(1)}$ *etc.* are the absolute activities[7] of the gaseous species, A_1 *etc.*, and of the critical complexes, $\ddagger(1)$ *etc.*, of steps, 1 *etc.*, respectively. By the use of above u's and referring to equation (4. v), the net rates, v_1 *etc.*, of respective steps are now given as

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

where

$$\left.\begin{array}{lll} f_1 \equiv a^{X_1}/a_{A_1}{}^{1/2}, & f_2 \equiv a^{X_2}/a_{A_2}\,, & f_3 \equiv a^{X_3}/a_{B_2}\,, \\ f_4 \equiv a^{X_4} a_{B_2}/a_{A_1}{}^{1/2} a_{A_2}\,, & f_5 \equiv a^{X_5}/a_{A_1}{}^{1/2} a_{B_2}\,, & \end{array}\right\} \quad (5.\,\mathrm{f})$$

is the fugacity of X_i ($i = 1, 2, \cdots$ 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

$$\left.\begin{array}{l} F_\alpha \equiv a_{B_3}/a_{A_1} a_{B_2}\,, \\ F_\beta \equiv a_{B_1}/a_{A_1} a_{A_2}\,, \\ F_\gamma \equiv a_{B_2} a_{B_4}/a_{B_1}\,, \end{array}\right\} \quad (5.\,\mathrm{F})$$

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

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

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

$(\mathrm{X}_i)_{eq}$; for instance,

$$kT\ln f_4=\mu^{\mathrm{X}_4}-(\mu_{\mathrm{A}_1}/2+\mu_{\mathrm{A}_2}-\mu_{\mathrm{B}_2})\,,$$

where $(\mathrm{X}_4)_{eq}=\mathrm{A}_1/2+\mathrm{A}_2-\mathrm{B}_2$. 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, $\varDelta G_s$, of step *s*. With respect to step 4, for instance, we have

$$kT\ln(f_1f_2-f_3f_4)=(\mu^{\mathrm{X}_1}+\mu^{\mathrm{X}_2})-(\mu^{\mathrm{X}_3}+\mu^{\mathrm{X}_4})=\varDelta G_4\,.$$

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.

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

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.*,

$$a_{\mathrm{A}_1}=P_{\mathrm{A}_1}U_{\mathrm{A}_1}$$

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

$$\left.\begin{aligned}&u_1=P_{\mathrm{A}_1}U_1\,, && u_2=P_{\mathrm{A}_2}U_2\,, && u_3=P_{\mathrm{A}_1}P_{\mathrm{A}_2}U_3\,,\\&u_4=P_{\mathrm{A}_1}{}^{1/2}P_{\mathrm{A}_2}U_4\,, && u_5=P_{\mathrm{B}_2}U_5\,, && u_6=P_{\mathrm{A}_1}{}^{1/2}P_{\mathrm{B}_2}U_6\,,\\&u_7=P_{\mathrm{A}_1}P_{\mathrm{B}_2}U_7\,, && u_8=(P_{\mathrm{A}_1}P_{\mathrm{A}_2}/P_{\mathrm{B}_2})\,U_8\,,\end{aligned}\right\}\quad(7.\,\mathrm{u})$$

where

$$\left.\begin{aligned}&U_1\equiv(kT/h)\,U_{\mathrm{A}_1}/a^{\ddagger(1)}, && U_2\equiv(kT/h)\,U_{\mathrm{A}_2}/a^{\ddagger(2)},\\&U_3\equiv(kT/h)\,U_{\mathrm{A}_1}U_{\mathrm{A}_2}/a^{\ddagger(3)}, && U_4\equiv(kT/h)\,U_{\mathrm{A}_1}{}^{1/2}U_{\mathrm{A}_2}/a^{\ddagger(4)},\\&U_5\equiv(kT/h)\,U_{\mathrm{B}_2}/a^{\ddagger(5)}, && U_6\equiv(kT/h)\,U_{\mathrm{A}_1}{}^{1/2}U_{\mathrm{B}_2}/a^{\ddagger(6)},\\&U_7\equiv(kT/h)\,U_{\mathrm{A}_1}U_{\mathrm{B}_2}/a^{\ddagger(7)}, && U_8\equiv(kT/h)\,U_{\mathrm{A}_1}U_{\mathrm{A}_2}/U_{\mathrm{B}_2}a^{\ddagger(8)},\end{aligned}\right\}\quad(7.\,\mathrm{U})$$

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

The F_α, F_β and F_γ given by equations (5. F) are, on the other hand, expressed as

$$\left.\begin{aligned} F_\alpha &= (P_{\mathrm{B}_3}/P_{\mathrm{A}_1}P_{\mathrm{B}_2})/K_\alpha, \\ F_\beta &= (P_{\mathrm{B}_1}/P_{\mathrm{A}_1}P_{\mathrm{A}_2})/K_\beta, \\ F_\gamma &= (P_{\mathrm{B}_2}P_{\mathrm{B}_4}/P_{\mathrm{B}_1})/K_\gamma, \end{aligned}\right\} \tag{7. F}$$

where K_α, K_β and K_γ 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.

$$1-F_\beta+\beta x_1x_2 = P_{\mathrm{A}_2}x_1+P_{\mathrm{A}_1}\beta x_2/(\alpha+\beta)+(\beta-\gamma)\,x_3/(\alpha+\beta), \tag{8. 1. x}$$

$$f_1 = \left(1-(\alpha+\beta)\,x_1/P_{\mathrm{A}_1}\right)^{1/2}, \qquad f_2 = 1-\beta x_2/P_{\mathrm{A}_2}, \tag{8. 1. f}$$

$$\left.\begin{aligned} P_{\mathrm{B}_2}\left(1-F_\alpha-(\alpha+\beta)/u_1\right) &= (\gamma-\alpha)\left(1+(\alpha+\beta)/u_1\right)x_5 \\ &\quad +(\alpha f_1/P_{\mathrm{A}_1}{}^{1/2})\,x_6+\alpha x_7/P_{\mathrm{A}_1}, \end{aligned}\right\} \tag{8. 2. x}$$

$$f_3 = 1+(\gamma-\alpha)\,x_5/P_{\mathrm{B}_2}, \qquad f_5 = (\alpha/u_7+F_\alpha)/f_1, \tag{8. 2. f}$$

$$\left.\begin{aligned} P_{\mathrm{A}_1}P_{\mathrm{A}_2}F_\beta(1-F_\gamma)-(\beta-\gamma)\,x_3-(\gamma-\alpha)\,P_{\mathrm{A}_1}P_{\mathrm{A}_2}F_\beta F_\gamma/u_5 \\ = P_{\mathrm{A}_1}{}^{1/2}\gamma f_1x_4+\gamma P_{\mathrm{B}_2}f_3x_8, \end{aligned}\right\} \tag{8. 3. x}$$

$$f_4 = (f_1f_2-\gamma/u_4)/f_3, \tag{8. 3. f}$$

where

$$x_s \equiv 1/U_s \qquad (s=1, 2, \cdots, 8). \tag{8. 4}$$

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, α *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[2] during the early 50 min are replaced by smoothed curves and their values at these four times of reaction are multiplied by 1.19×10^{-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,

$$P_{\mathrm{B}_4} = P_{\mathrm{B}_2}+P_{\mathrm{B}_3}$$

and

$$P_{\mathrm{A}_1} = 17.85-(P_{\mathrm{B}_1}+P_{\mathrm{B}_3}+P_{\mathrm{B}_4})\ \mathrm{mmHg}.$$

As seen from reactions (4. R), their steady rates, α, β and γ, are given as

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[2)].

time min	cyclo-pentanone (A_1)	cyclo-pentanol (B_1)	cyclo-pentene (B_2)	cyclo-pentane (B_3)	water (B_4)	hydrogen (A_1)
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	α	β	γ	F_α	F_β	F_γ
min	mmHg/min					
20	0.0108	0.0120	0.0131	1.91915×10^{-8}	1.0	1.54229×10^{-3}
25	0.0104	0.0113	0.0123	1.78039×10^{-8}	1.0	2.09279×10^{-3}
30	0.0099	0.0105	0.0116	1.67210×10^{-8}	1.0	3.15801×10^{-3}

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

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_α and K_γ 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)[8)] as

$$K_\alpha = 1.57305\times10^6\,\text{mmHg}^{-1}, \quad K_\gamma = 1.5870\times10^3\,\text{mmHg}, \tag{8. K}$$

respectively. There is no data available for evaluation of K_β. Provided that K_β is close to the equilibrium constant of the hydrogenation of cyclohexanone to cyclohexanol[9)], we have

$$K_\beta = 1.112\times10^{-2}\,\text{mmHg}^{-1},$$

which is close to the value,

$$P_{B_1}/P_{A_1}P_{A_2} = 1.06\times10^{-2}\,\text{mmHg}^{-1},$$

estimated from the date of Table 1 at $t=20$, 25 or 30 min, and, thus, F_β is approximated by unity, which means the equilibrium of the second reaction of (4. R) as suggested by KEMBALL and STODDART[2]. The value of F_α, F_β and F_γ evaluated according to equations (7. F) and (8. K) are given in Table 2.

Introducing the three sets of values of α, β, 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

$$\left.\begin{aligned} x_1 &\equiv 1/U_1 = 6.87\times10^{-4}, \\ x_2 &\equiv 1/U_2 = 3.91\times10^{-5}, \\ x_3 &\equiv 1/U_3 = 1.24\times10^{-2}, \end{aligned}\right\} \qquad (9.\,\mathrm{x})$$

and further from equations (8. 1. f)

$$f_1 = 0.99999956\,, \qquad f_2 = 0.99999898 \qquad (9.\,\mathrm{f})$$

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

$$\left.\begin{aligned} x_5 &\equiv 1/U_5 = 2.06\times10^{2}, \\ x_6 &\equiv 1/U_6 = -8.73\times10^{2}, \\ x_7 &\equiv 1/U_7 = 5.00\times10^{3}, \end{aligned}\right\} \qquad (10.\,\mathrm{x})$$

and

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

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 apparenlty negative x is considered to be nearly zero. There is some support of this approximation with respect to x_6 as discussed later. Assuming $x_6 \cong 0$, we have from equation (8. 2. x) and the experimental data of Table 1 at $t=20$ and 25 min that

$$x_5 = 2.03\times10^{2}, \quad x_7 = 1.37\times10^{3} \qquad (x_6 \cong 0)\,, \qquad (11.\,\mathrm{x})$$

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

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

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

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

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

$$x_4 = 1.83\times10^2 \quad \text{and} \quad x_8 = -1.26\times10^2.$$

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

$$x_4 \equiv 1/U_4 = 9.70\times10^2 \qquad (x_8 \equiv 1/U_8 \cong 0), \qquad (12.\ x)$$

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

$$f_4 \cong F_\gamma = 2.093\times10^{-3} \qquad (t=25\ \text{min}). \qquad (12.\ f)$$

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 $x_8 \cong 0$ 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	1.4536×10^3	u_1	2.4860×10^4	f_1	0.99999956
U_2	2.5606×10^4	u_2	1.1710×10^4	f_2	0.99999898
U_3	8.0744	u_3	6.3164×10^2	f_3	1.864
U_4	1.0308×10^{-3}	u_4	1.9502×10^{-3}	f_4	2.093×10^{-3}
U_5	4.9169×10^{-3}	u_5	2.1200×10^{-3}	f_5	1.864
U_6	∞	u_6	∞		
U_7	7.2930×10^{-4}	u_7	5.5805×10^{-3}		
U_8	∞	u_8	∞		

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 $x_6 \cong 0$ is in conformity with the conclusion on catalytic hydrogenation of monoolefines[5)] 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 the present analysis, the kinetic behaviour of the hydrogenolysis can be consistently discussed as follows.

As discussed in the previous paper[1] 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, α, β or γ, 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. ν) of the steady state condition (3. ν). 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_β 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[2] mentiond 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[2] for the formation of 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[2)].

The values of U's may vary with the progress of reaction due to the change of its factor, $a^{\ddagger(s)}$, caused by variation of the interaction of $\ddagger$(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 $F_\gamma \cong 1$, hence f_4 is close to unity on account of that $\gamma = v_8 = v_8(f_1f_4 - F_\beta F_\gamma)$ is small and finite, whereas $u_8 \cong \infty$, $f_1 \cong 1$ and $F_\beta = 1$. 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_γ, 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 $v_4 = u_4(f_1f_2 - f_3f_4) \cong 0$, where $f_1 \cong 1$ and $f_2 \cong 1$. 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 pressure dependence of the steady rate, α, 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, $\alpha = V_{B_3}$, 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,

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

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[2)] 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[2)] 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 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[2] 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[1] 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.

References

1) K. MIYAHARA and S. YOKOYAMA, This Journal, **19**, 127 (1971).
2) C. KEMBALL and C. T. H. STODDART, Proc. Roy. Soc. **A 246**, 521 (1958).
3) C. KEMBALL and C. T. H. STODDART, *ibid.* **A 241**, 208 (1957).
4) K. NAGAI and K. MIYAHARA, to be published.
5) J. HORIUTI and K. MIYAHARA, *Hydrogenation of Ethylene on Metallic Catalysts*, NSRDS-NBS 13, National Bureau of Standards, U.S.A., 1968.
6) J. HORIUTI and T. NAKAMURA, *Advances in Catalysis* (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 1, Academic Press, New York and London, 1967.
7) R. H. FOWLER and E. A. GUGGENHEIM, *Statistical Thermodynamics*, Cambridge Univ. Press, p. 66, 1939.
8) LANDOLT-BÖRNSTEIN Tabellen, Auflage 6, Band II, Teil 4, 1962.
9) A. H. CUBBERLEY and M. B. MULLER, J. Amer. Chem. Soc. **69**, 1535 (1947).