Kinetics of Liquid-phase Hydrogenation of Aliphatic α,β-Unsaturated Aldehyde over Raney Cobalt Catalyst

Kazuhiko HOTTA and Teruo KUBOMATSU
The Osaka Municipal Technical Research Institute, Kita-ku, Osaka

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Kinetic studies on the hydrogenation of 2-methyl-2-pentenal (UD) over the Raney cobalt catalyst were performed at temperatures ranging from 10 to 40°C in *n*-hexane. The products were found to be 2-methylpentan-1-ol (SA), 2-methyl-2-penten-1-ol (UA) and 2-methylpentanal (SD). The initial rates of the formation of SA(r_{SA}), SD(r_{SD}), and UA(r_{UA}) were determined in the concentrations of UD(C_{UD}), 0.026 − 0.263 mol/*l*. It was found by kinetic analysis that ($r_{SA}+r_{SD}$) was represented by a Langmuir-type rate equation and r_{UA} by another one. The rate equations which fitted the rate data are as follows.

$$r_{SA} + r_{SD} = \frac{1.1\times 10^{10}e^{-15200/RT}C_{UD}}{(1+4.4\times 10^{5}e^{-7500/RT}C_{UD})^2}$$

$$r_{UA} = \frac{1.2\times 10^{8}e^{-13500/RT}C_{UD}}{(1+9.3\times 10^{3}e^{-5600/RT}C_{UD})^2}$$

A mechanism in which the formation of SA and SD and that of UA proceed through different types of adsorbed UD was proposed. The adsorbed species in enol form and that in keto form were considered with respect to the formation of SA and SD. Activation energies for the formation of SA plus SD and of UA were determined to be 7.7 and 7.9 kcal/mol, respectively. The selectivity defined as the ratio of r_{SA} to ($r_{SA}+r_{SD}$) was found to increase with the increase of the surface coverage of hydrogen.

The vapor phase hydrogenation of 2-ethyl-2-hexenal over the supported copper catalyst was studied by Tanaka and Yada.[1] It was found that each reaction order with respect to the carbon-carbon double bond and the aldehyde group was unity. The hydrogenation of crotonaldehyde over the Raney copper-cadmium catalyst has also been kinetically studied in the vapor phase by Yada and Kudo.[2] In order to determine the rate constant, they assumed that the reaction order with respect to the reactant was unity, and neglected to consider the adsorption factor.

We have studied the liquid phase hydrogenation of α,β-unsaturated aldehydes over the Raney nickel catalyst with or without modifiers and have found that the products were saturated aldehydes and alcohols and that unsaturated alcohol was not produced.[3] Over the Raney cobalt catalyst, on the other hand, unsaturated alcohol was found to be formed with saturated aldehyde and alcohol. There have been only few kinetic studies on such a complicated reaction system in the liquid phase, consisting of both parallel and successive reactions.

It is the purpose of this paper to elucidate the kinetic behavior of the hydrogenation of 2-methyl-2-pentenal over the Raney cobalt catalyst in *n*-hexane. The kinetics was found to be best fitted to the rate equation based on the Langmuir-Hinshelwood mechanism. A detailed discussion is also made on the mechanism of the reactions.

Experimental

Catalyst. A commercial Raney cobalt-aluminum alloy (Co:50 wt%) was developed with a 15% sodium hydroxide solution at 50°C for 1 hr. The sample was washed with minimum volume of distilled water until the washings became neutral, then 5 times with 2-propanol, and 10 times with *n*-hexane in a hydrogen atomsphere. *n*-Hexane was then evaporated with hydrogen stream. The resulting catalyst, 540 mg (Co: *ca.* 500 mg), in dry form was weighed and stored in *n*-hexane under a hydrogen atmosphere. Decrease in the activity of the catalyst could be ignored within 4 weeks after the preparation.

Apparatus and Procedure. The catalyst, 540 mg, and *n*-hexane were put into a glass reaction vessel with a rubber-stoppered branch tube, and then the reaction vessel was equipped with a metal flange with three needle valves and with a mechanically sealed stirrer. After replacing air with hydrogen by making use of valve(1), the reactor was immersed in a constant temperature water bath controlled to ±0.05°C. Hydrogen was bubbled into the catalyst-solvent system through valve (2). In order to carry out the reaction under normal pressure, hydrogen was exhausted through valve (3) to atmosphere through a bubble counter. The catalyst-solvent system was stirred with 500 rpm in the hydrogen flow to saturate the catalyst with hydrogen. The reactant to be hydrogenated was then injected to this system. The total volume of the reactant and the solvent was kept to 50 m*l*. When the reactant was injected to the catalyst-solvent-hydrogen system, rapid absorption of hydrogen took place. The rate dropped to almost constant after 30 sec. Thus, the reaction was considered to reach the steady state within 30 sec after the injection of the reactant.

The total rate of the formation of the products was found to increase and become saturated with increased stirring. Hydrogenation was carried out under the conditions where the rate is independent of stirring. The maximum of the apparent activation energy observed in this study is 10 kcal/mol, indicating that diffusional process plays no important role under the conditions adopted.

The reaction mixture was sampled from the branch tube through a rubber stopper and the composition of the liquid phase was determined by glc employing a column packed with 20% PEG 6000/C-22.

Materials. *n*-Hexane was purified by hydrogenating reducible impurities. Cylinder hydrogen and 2-propanol were used without further purification. 2-Methyl-2-pentenal, pre-

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[1] T. Tanaka and S. Yada, *Kagaku Kogaku*, **21**, 721 (1957).

[2] S. Yada and S. Kudo, *Shokubai*, **6**, 85 (1964).

[3] K. Hotta and T. Kubomatsu, Preprints for the 20th Annual Meeting of the *Chem. Soc. Japan* (Tokyo, 1967), No. 11303.

pared from propionaldehyde and stored in portions of (0.2—1.8) m*l*, in sealed glass ampoules under a nitrogen atmosphere at −15°C, was 99% up pure.

Results

Determination of the Initial Rate. A representative of the change in product pattern as a function of reaction time of the hydrogenation of 2-methyl-2-pantenal (UD) over the Raney cobalt catalyst is shown in Fig. 1. The plots shown by the symbol ♁ are from a catalyst prepared in one batch and those by the symbol ♀ from a catalyst in another batch. Reproducibility in the rate measurement is satisfactory.

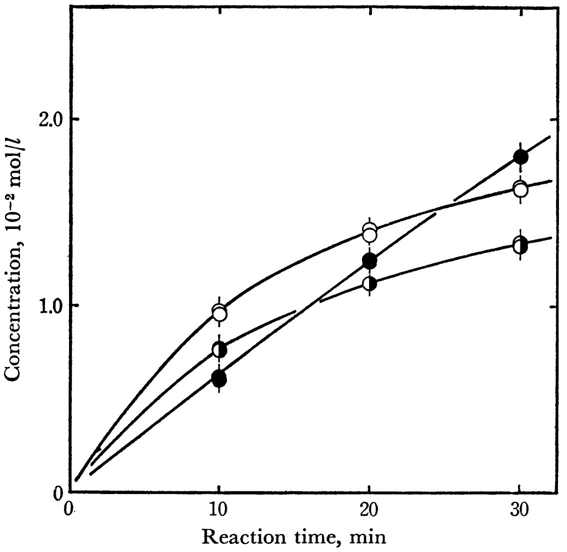

Fig. 1. Product concentration-time curves at 40°C, C_{UD}, 0.105 mol/l; SD, ○; SA, ●; UA, ◑

The rate of formation of the saturated aldehyde, 2-methylpentanal (SD), and that of the unsaturated alcohol, 2-methyl-2-penten-1-ol (UA), decrease gradually with reaction time. The rate of formation of the saturated alcohol, 2-methylpentan-1-ol (SA), is practically constant. It was also observed that the rate of formation of SA, however, showed a negative order dependence at higher concentration of UD and at lower reaction temperature. This indicates that (i) the hydrogenation of UD consists of a consecutive reaction which proceeds *via* SD or/and UA, and (ii) SA is the terminal product.

Isomerization from UA to SD and the dehydrogenation of SA and UA were not observed.

It was found that each product concentration-time curve could be represented by the third order equation as shown by the solid line in Fig. 1:

$$C = Xt^3 + Yt^2 + Zt \tag{1}$$

where C denotes the concentration of a product at the reaction time t, and X, Y, Z are constants. The rate at t is given by differentiating Eq. (1) with respect to t, *viz.*,

$$\frac{dC}{dt} = 3Xt^2 + 2Yt + Z \tag{2}$$

Thus the initial rate is given by

$$\left(\frac{dC}{dt}\right)_{t=0} = Z$$

Therefore the initial rate is the rate at the reaction time $t=0$, obtained by extrapolation from the rate of formation-time curve experimentally determined in the period in which the reaction proceeds in steady state. The kinetic analysis is made with the assumption that the reaction proceeds in steady state even at the reaction time $t=0$.

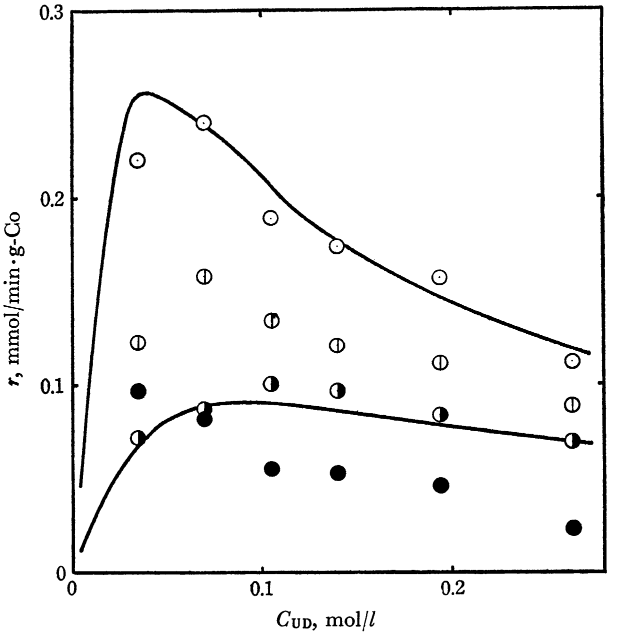

Fig. 2. Concentration dependence of the initial rate of the formation of, SD, ⦶; SA, ●; SA+SD, ○; UA, ◑, at 40°C.

Concentration Dependence of the Initial Rate: The initial rate of formation of SA, SD, and UA were plotted against the concentration of UD in Fig. 2. The curves for SD and UA have maxima, while the one for SA showed a progressive decrease with increasing the concentration of UD. This suggests that the reaction proceeds by the Langmuir-Hinshelwood mechanism, in which hydrogen and UD are adsorbed competitively. The rate equation corresponding to the mechanism is

$$r = k\theta_H\theta_{UD} \tag{3}$$

where k denotes the rate constant of the surface reaction, θ_H, the surface coverage of hydrogen, and θ_{UD}, that of UD. The following equation can be derived from Eq. (3) as has been reported by Kishida and Teranishi[4]

$$r = \frac{kbC_{UD}}{(1+bC_{UD})^2} \tag{4}$$

where C_{UD} denotes the concentration of UD, and b the ratio of the adsorption equilibrium constant of UD to that of hydrogen, divided by the liquid phase concentration of hydrogen, *i.e.* $b=K_{UD}/K_H \cdot C_H$, and called adsorption coefficient. When the rate measurement is carried out under a constant pressure of hydrogen, and the solubility of hydrogen is considered to be independent of the composition of reaction mixture

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[4] S. Kishida and S. Teranishi, *J. Catal.*, **12**, 90 (1968).

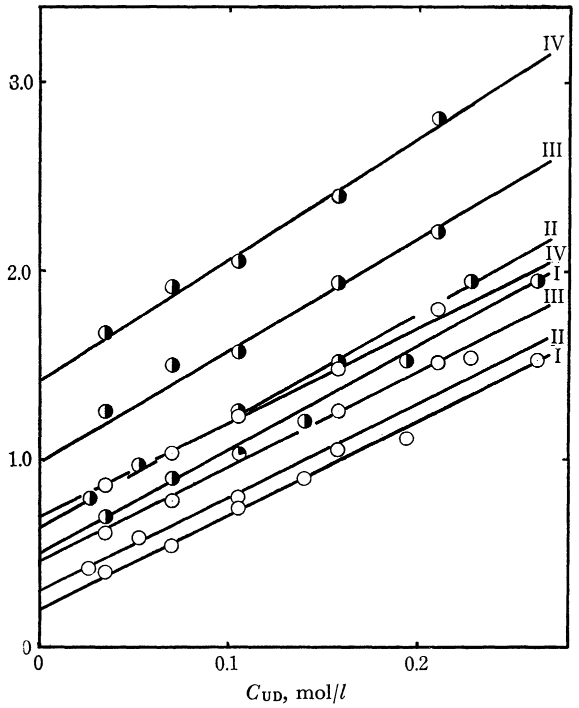

Fig. 3. $(C_{UD}/r)^{1/2}$ *vs.* C_{UD} plots for, $r_{SA}+r_{SD}$, ○; r_{UA}, ◐ at 40°C, I; 30°C, II; 20°C, III; 10°C, IV.

the adsorption coefficient b has a constant value at a given temperature. The adsorption of n-hexane as a solvent is neglected. The re-adsorption of products can be neglected in the initial rate treatment performed in this study.

Rearranging Eq. (4), we obtain

$$\left(\frac{C_{UD}}{r}\right)^{1/2} = \frac{1}{(kb)^{1/2}} + \left(\frac{b}{k}\right)^{1/2}\cdot C_{UD} \qquad (5)$$

This gives a linear relation between $(C_{UD}/r)^{1/2}$ and C_{UD}. In Fig. 3, plots of $(C_{UD}/r_{UA})^{1/2}$, and $(C_{UD}/(r_{SA}+r_{SD}))^{1/2}$ *vs.* C_{UD} are shown, where r_{UA}, r_{SA}, and r_{SD} denote the initial rates of formation of UA, SA, and SD, respectively. These plots obvioulsy give straight lines. We see that the plot of $(C_{UD}/r_{SA})^{1/2}$ *vs.* C_{UD} deviates from a straight line. This trend of plots can be interpreted as indicating that SA and SD were formed through the same adsorbed species. The kinetic parameters k and b were determined from the plots in Fig. 3, and are given in Table 1. The behavior of the concentration dependence of the initial rate of formation of SA plus SD and that of UA, employing such values of k and b, reveal satisfactory agreement between the experimental data and the calculated values, as shown by solid lines in Fig. 2.

TABLE 1. KINETIC PARAMETERS

	With respect to the formation of SA+SD		UA	
Temperature (°C)	k (mmol/min·g-Co)	b (l/mol)	k	b
40	1.0	25	0.38	11
30	0.68	17	0.28	9.0
20	0.44	11	0.17	6.1
10	0.29	7.1	0.11	4.5
Temperature coefficient (kcal/mol)	7.7	7.5	7.9	5.6
Frequency factor (mmol/min·g-Co)	2.5×10^4	—	1.3×10^4	—
Pre-exponential factor (l/mol)	—	4.4×10^5	—	9.3×10^3

The activation energies for the formation of SA plus SD and of UA were 7.7 and 7.9 kcal/mol, respectively. The values are considered to the reasonable compared with those reported by other workers.[5,6] The temperature coefficients of b were also determined to be 7.5 and 5.6 kcal/mol, for SA plus SD and for UA,

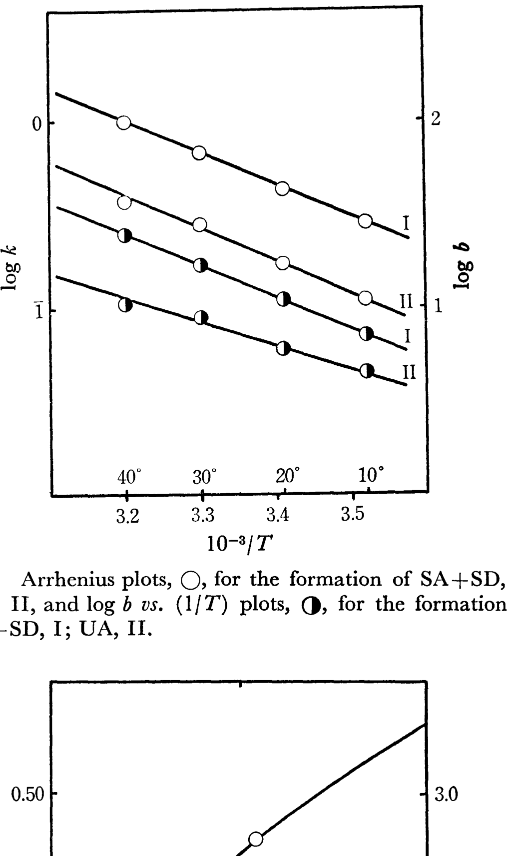

Fig. 4. Arrhenius plots, ○, for the formation of SA+SD, I; UA, II, and log b *vs.* $(1/T)$ plots, ◐, for the formation of SA+SD, I; UA, II.

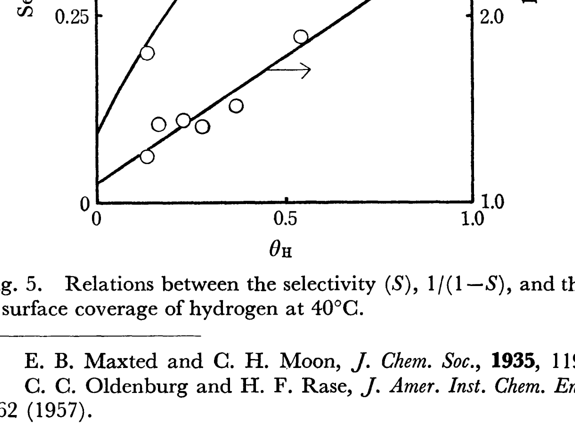

Fig. 5. Relations between the selectivity (S), $1/(1-S)$, and the surface coverage of hydrogen at 40°C.

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5) E. B. Maxted and C. H. Moon, *J. Chem. Soc.*, **1935**, 1190.

6) C. C. Oldenburg and H. F. Rase, *J. Amer. Inst. Chem. Eng.*, **3**, 462 (1957).

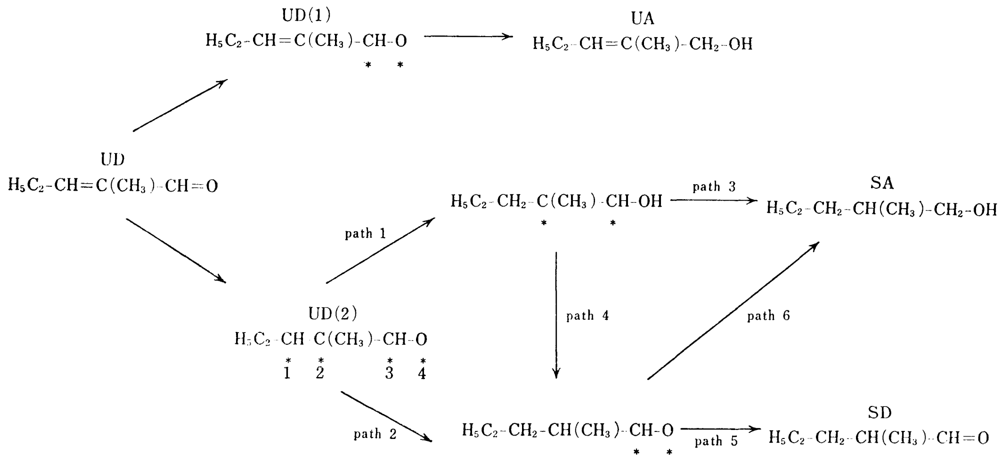

Fig. 6. Scheme of the hydrogenation mechanism.

respectively. This indicates that hydrogen is adsorbed more strongly than UD. The frequency factors of the rate constants for SA plus SD and for UA were determined to be 2.5×10^4 and 1.3×10^4 mmol/min·g-Co, respectively. The pre-exponential factors of the adsorption coefficients for SA plus SD and for UA were also determined to be 4.4×10^5 and 9.3×10^3 l/mol, respectively. Plots of the logarithm of k and b *vs.* the reciprocal of absolute temperature are shown in Fig. 4.

The relation between selectivity and surface coverage of hydrogen can be calculated employing the kinetic parameters obtained above. Selectivity S is defined as the ratio of r_{SA} to $(r_{SA}+r_{SD})$ and the surface coverage of hydrogen is calculated by the equation $\theta_H=1/(1+bC_{UD})$. The result at 40°C is shown in Fig. 5. It is found that selectivity increases with the increase of hydrogen coverage.

Discussion

The hydrogenation mechanism which is considered to be consistent with the experimental results above mentioned is shown in Fig. 6. Two different types of adsorbed UD are considered in the mechanism. Formation of UA proceeds through UD (1), and that of SA and SD occurs through UD (2). The adsorbed species UD (2) is hydrogenated by 1,2 addition (path 2) to form the adsorbed species in keto form and by 1,4 addition (path 1) to form that in enol form. The reaction mechanism which involves both 1,2 and 1,4 additions of hydrogen has been proposed by McQuillin *et al.*[7] The adsorbed enol species is hydrogenated to SA or isomerized to the adsorbed keto species, while the isomerization from the latter to the former does not occur as reported by Badin and Pacsu.[8]

If UD is adsorbed competitively as UD (1) and UD(2) on the same catalyst site and reacts with adsorbed hydrogen, the rate equations for the formation of UA and of SA plus SD can be derived as follows.

$$r_{UA}=\frac{k_{UD(1)}b_{UD(1)}C_{UD}}{\{1+(b_{UD(1)}+b_{UD(2)})C_{UD}\}^2} \tag{6}$$

$$r_{SA}+r_{SD}=\frac{k_{UD(2)}b_{UD(2)}C_{UD}}{\{1+(b_{UD(1)}+b_{UD(2)})C_{UD}\}^2} \tag{7}$$

where $k_{UD}(1)$ denotes the rate constant for the formation of UA, $k_{UD}(2)$ that of SA plus SD, $b_{UD}(1)$ the adsorption coefficient of UD(1), and $b_{UD}(2)$ that of UD(2). Rearranging these equations, we have

$$\left(\frac{C_{UD}}{r_{UA}}\right)^{1/2}=\frac{1}{(k_{UD(1)}b_{UD(1)})^{1/2}}+\frac{b_{UD(1)}+b_{UD(2)}}{(k_{UD(1)}b_{UD(1)})^{1/2}}\cdot C_{UD} \tag{8}$$

$$\left(\frac{C_{UD}}{r_{SA}+r_{SD}}\right)^{1/2}=\frac{1}{(k_{UD(2)}b_{UD(2)})^{1/2}}+\frac{b_{UD(1)}+b_{UD(2)}}{(k_{UD(2)}b_{UD(2)})^{1/2}}\cdot C_{UD} \tag{9}$$

which give linear relations between $(C_{UD}/r_{UA})^{1/2}$, $(C_{UD}/(r_{SA}+r_{SD}))^{1/2}$ and C_{UD}. Then relations between the slopes and the intercepts of the plots of Eqs. (8) and (9) are obtained as follows.

$$x_1/y_1=b_{UD(1)}+b_{UD(2)}$$
$$x_2/y_2=b_{UD(1)}+b_{UD(2)}$$

where x_1 denotes the slope of the plot for r_{UA}, y_1 the intercept of that for r_{UA}, x_2 the slope of the plot for $(r_{SA}+r_{SD})$, and y_2 the intercept of that for $(r_{SA}+r_{SD})$. This indicates that the ratio of the slope and the intercept of the Langmuir-plots for r_{UA} and for $(r_{SA}+r_{SD})$ have the same value. It was found, however, from the plots in Fig. 3 that the values of the term, x/y, were not identical for both lines. This suggests that the part of the catalyst surface on which UD(1) is hydrogenated differs from that on which UD(2) is hydrogenated, and the formation of UA and that of SA plus SD can be treated seperately.

Following discussion is made to analyze semi-quantitatively the result shown in Fig. 5 on the basis of the mechanism assumed. According to the mechanism, the rate of the formation of SA and SD can be written as

$$r_{SA}=k_6\theta_H\theta_{keto}+k_3\theta_H\theta_{enol} \tag{10}$$

$$r_{SD}=k_5\theta_{keto} \tag{11}$$

where k_i denotes the rate constant whose subscript i represents each reaction path shown in Fig. 6, and θ the surface coverage. Equating the rates of the formation and the removal of the adsorbed enol species and those of the adsorbed keto species, we get

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[7] F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, **1963**, 5996.

[8] E. J. Badin and E. Pacsu, *J. Amer. Chem. Soc.*, **66**, 1963 (1944).

$$k_1\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)} = k_3\theta_{\mathrm{H}}\theta_{\mathrm{enol}} + k_4\theta_{\mathrm{enol}}$$

$$k_2\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)} + k_4\theta_{\mathrm{enol}} = k_6\theta_{\mathrm{H}}\theta_{\mathrm{keto}} + k_5\theta_{\mathrm{keto}}$$

where the re-adsorption of products were neglected in the "initial rate" treatment, and the fraction of the surface coverage of the adsorbed enol species and that of the adsorbed keto species are obtained:

$$\theta_{\mathrm{enol}} = \frac{k_1\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)}}{k_3\theta_{\mathrm{H}}+k_4} \tag{12}$$

$$\theta_{\mathrm{keto}} = \frac{k_2(k_3\theta_{\mathrm{H}}+k_4)+k_1k_4}{(k_6\theta_{\mathrm{H}}+k_5)(k_3\theta_{\mathrm{H}}+k_4)}\cdot\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)} \tag{13}$$

Substituting Eqs. (12) and (13) into Eq. (10), the rate of formation of SA is obtained as

$$r_{\mathrm{SA}} = \left[\frac{k_1k_3\theta_{\mathrm{H}}}{k_3\theta_{\mathrm{H}}+k_4} + \frac{k_2k_6\theta_{\mathrm{H}}(k_3\theta_{\mathrm{H}}+k_4)+k_1k_4k_6\theta_{\mathrm{H}}}{(k_3\theta_{\mathrm{H}}+k_4)(k_6\theta_{\mathrm{H}}+k_5)}\right] \times \theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)} \tag{14}$$

The rate of formation of SA is divided into three terms. The first term represents it through the reaction path 1—3 *via* the adsorbed species in enol form, the second term through the path 2—6, and the third term through the path 1—4—6. Equation (14) is then rewritten as

$$r_{\mathrm{SA}} = (r_{\mathrm{SA}})_{1-3} + (r_{\mathrm{SA}})_{2-6} + (r_{\mathrm{SA}})_{1-4-6} \tag{15}$$

Addition of Eqs. (10) and (11) leads to

$$r_{\mathrm{SA}} + r_{\mathrm{SD}} = (k_6\theta_{\mathrm{H}}+k_5)\cdot\theta_{\mathrm{keto}} + k_3\theta_{\mathrm{H}}\theta_{\mathrm{enol}} \tag{16}$$

Insertion of Eqs. (12) and (13) into Eq. (16) gives, after rearrangement.

$$r_{\mathrm{SA}} + r_{\mathrm{SD}} = (k_1+k_2)\cdot\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)} \tag{17}$$

Selectivity S is also derived as follows.

$$S = \frac{r_{\mathrm{SA}}}{r_{\mathrm{SA}}+r_{\mathrm{SD}}} = \frac{k_1k_3\theta_{\mathrm{H}}(k_6\theta_{\mathrm{H}}+k_5)+k_1k_4k_6\theta_{\mathrm{H}}+k_2k_6\theta_{\mathrm{H}}(k_3\theta_{\mathrm{H}}+k_4)}{(k_3\theta_{\mathrm{H}}+k_4)(k_6\theta_{\mathrm{H}}+k_5)(k_1+k_2)} \tag{18}$$

Equation (18) can be rearranged as

$$S = 1 - \frac{\left(\frac{k_2\theta_{\mathrm{H}}}{k_1+k_2}+\frac{k_4}{k_3}\right)\cdot\frac{k_5}{k_6}}{\left(\theta_{\mathrm{H}}+\frac{k_5}{k_6}\right)\left(\theta_{\mathrm{H}}+\frac{k_4}{k_3}\right)} \tag{19}$$

After rearrangement, Eq. (19) can be reduced as follows. (i) If $k_4/k_3=0$, then

$$\frac{1}{1-S} = \frac{k_6}{k_5}\cdot\frac{k_1+k_2}{k_2}\cdot\theta_{\mathrm{H}} + \frac{k_1+k_2}{k_2} \tag{20}$$

and (ii) if $k_2/(k_1+k_2)=1$, then

$$\frac{1}{1-S} = \frac{k_6}{k_5}\cdot\theta_{\mathrm{H}} + 1 \tag{21}$$

A linear relation between $1/(1-S)$ and θ_{H} was experimentally found as shown in Fig. 5. The values of the slope and the intercept determined by the least square method were 1.36 and 1.10, respectively. Thus we have from Eq. (20) $k_2/(k_1+k_2)=1/1.10$, $k_5/k_6=1.10/1.36$. Hence $k_1=0.1k_2$.

As the rate constant of 1,2 addition (k_2) is much larger than that of 1,4 addition (k_1), and the rate constant of reaction path 4 is negligibly small compared with that of reaction path 3, SD is considered to be formed through the adsorbed keto species *via* path 2—5.

Employing the values of the rate constants, the three terms in Eq. (15) can be calculated referring to Eq. (14). The first and second term are reduced as

$$(r_{\mathrm{SA}})_{1-3} = 0.1k_2\cdot\theta_{\mathrm{H}}\theta_{\mathrm{UD}(2)}$$

$$(r_{\mathrm{SA}})_{2-6} = k_2\theta^2{}_{\mathrm{H}}\theta_{\mathrm{UD}(2)}/(\theta_{\mathrm{H}}+0.81)$$

The third term is negligibly small since k_4 is zero. Thus a fraction of $(r_{\mathrm{SA}})_{2-6}$ over r_{SA} is

$$(r_{\mathrm{SA}})_{2-6}/r_{\mathrm{SA}} = 0.91\theta_{\mathrm{H}}/(\theta_{\mathrm{H}}+0.073) \tag{22}$$

It is found from Eq. (22) that the contribution of paths 2—6 to the formation of SA increases with the increase of hydrogen coverage. It can therefore be said that the formation of SA occurs dominantly through the adsorbed enol species *via* paths 1—3 at lower hydrogen coverage and through the adsorbed keto species *via* paths 2—6 at higher hydrogen coverage.

The fact that the selectivity, $r_{\mathrm{SA}}/(r_{\mathrm{SA}}+r_{\mathrm{SA}})$, increases with the increase of hydrogen coverage as shown in Fig. 5 can be interpreted as due to the increase of the fraction of adsorbed keto species consumed for the formation of SA.