## NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3566—3567 (1973)

# Modifying Effect of Acetic Acid or Triphenylphosphine on the Raney Cobalt Catalyst in the Liquid-phase Hydrogenation of an Aliphatic α,β-Unsaturated Aldehyde

Kazuhiko HOTTA and Teruo KUBOMATSU
*The Osaka Municipal Technical Research Institute, Kita-ku, Osaka 530*

(Received November 13, 1972)

In our previous papers,[1,2] we have reported that, in the hydrogenation of the α,β-unsaturated aldehyde, 2-methyl-2-pentenal(UD), over the Raney cobalt catalyst with or without modifiers, the products are the saturated aldehyde 2-methylpentanal(SD), saturated alcohol 2-methylpentan-1-ol(SA), and unsaturated alcohol 2-methyl-2-penten-1-ol(UA), and that the initial rates of formation of the three products, $r_{SD}$, $r_{SA}$, and $r_{UA}$, can be represented by the following Langmuir-type rate equations:

$$r_{SD} + r_{SA} = k_1 b_1 C_{UD}/(1+b_1 C_{UD})^2 \tag{1}$$

$$r_{UA} = k_2 b_2 C_{UD}/(1+b_2 C_{UD})^2 \tag{2}$$

where $k$ and $b$ denote the rate constant of the surface reaction and the adsorption parameter for UD and hydrogen[3] respectively; where the subscripts 1 and 2 represent the formation of SD and SA and that of UA respectively, and where $C_{UD}$ refers to the liquid-phase concentration of UD. There it has also been shown that $k_1$ decreases with an increase in the amounts of Mn- and $CoCl_2$ added, while $k_2$ does not change or increases with the addition of a small amount of the modifiers.

In the present note, the variation in the kinetic parameters with the amounts of added acetic acid (AcOH) and triphenylphosphine($PPh_3$) is examined. The variation of $k_1$ and $k_2$ over the AcOH-modified catalyst is found to be similar to that over the $MnCl_2$- and $CoCl_2$-modified catalysts, but both $k_1$ and $k_2$ are decreased by the addition of $PPh_3$. It can be concluded that the acidic modifiers, such as AcOH, $MnCl_2$, and $CoCl_2$, promote the formation of UA.

### Experimental

The Raney cobalt catalyst was prepared as has previously been reported.[1] The catalyst was modified by injecting a hexane solution of AcOH or $PPh_3$ to the catalyst–hexane–hydrogen system and by stirring the mixture.

The rate measurements were carried out as has been reported in a previous paper.[1]

### Results

The products of the reaction were found to be SD, SA, and UA. The dependence of the initial rates on $C_{UD}$ over the AcOH-modified catalyst are shown for $r_{SD}$ and $r_{SA}$ in Fig. 1, and for $r_{UA}$ in Fig. 2.

Since the formation of SD and SA and that of UA can be treated separately,[1,2] the rate data in Figs. 1 and 2 were analyzed by means of Eqs. (1) and (2) respectively, and the kinetic parameters, $k_1$, $k_2$, $b_1$, and

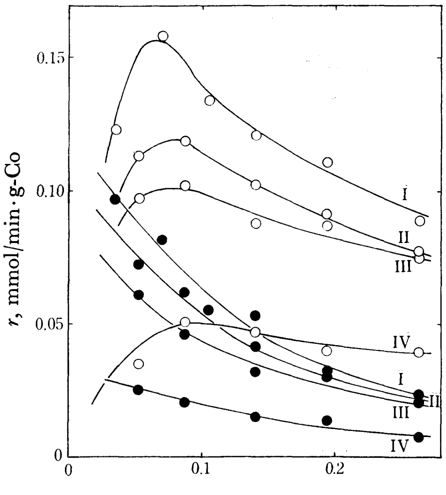

Fig. 1. Concentration dependence of the initial rate of formation of SD, ○; SA, ●, in the presence of AcOH of 0.0, I; 0.035, II; 0.070, III; 0.175 mmol/g-Co, IV at 40 °C.

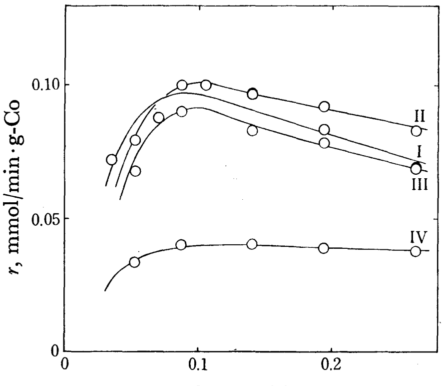

Fig. 2. Concentration dependence of the initial rate of formation of UA. Same notations as in Fig. 1.

---

[1] K. Hotta and T. Kubomatsu, This Bulletin, **44**, 1348 (1971).

[2] *Idem, ibid.*, **45**, 3118 (1972).

[3] The accurate definition of $b$ is: $b=K_{UD}/(K_H \cdot C_H)$, where $C_H$ refers to the liquid phase concentration of hydrogen and is assumed to be constant at a given temperature, and where $K_{UD}$ and $K_H$ denote the adsorption equilibrium constants of UD and hydrogen, respectively.

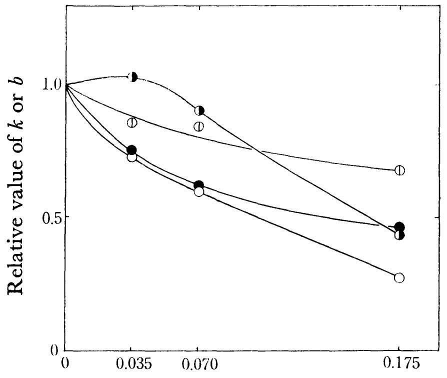

Fig. 3. Variation of the rate constant and adsorption parameter with the amount of AcOH, $k_1$, ○; $k_2$, ◑; $b_1$, ●; $b_2$, ⦶.

$b_2$, were evaluated to see how the values of these parameters vary with the modification.

The values of the kinetic parameters/values without modifier are plotted against the amount of AcOH added in Fig. 3. The rate constant for the formation of SD and SA, $k_1$, and the adsorption parameters, $b_1$ and $b_2$, were found to decrease upon the addition of AcOH, while $k_2$ did not change upon the first addition of a small amount of AcOH, but then began to decrease upon further addition.

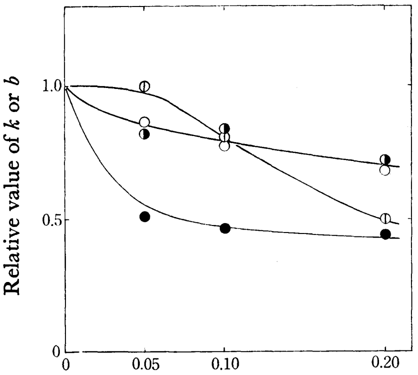

Fig. 4. Variation of the rate constant and adsorption parameter with the amount of $PPh_3$. Same notations as in Fig. 3.

The results obtained on the catalyst modified with $PPh_3$ are also shown in Fig. 4. It was found that $k_2$ as well as $k_1$ and $b_1$ decreased when the catalyst was modified with $PPh_3$, and that $b_2$ did not change on the first addition of a small amount of $PPh_3$.

## Discussion

The behavior of the two kinetic parameters for the formation of SD and SA ($k_1$ and $b_1$) over the AcOH- and $PPh_3$-modified catalysts are found to be similar to each other.

It is interesting that the variation in the kinetic parameters for the formation of UA ($k_2$ and $b_2$) over the AcOH-modified catalyst is different from that over the $PPh_3$-modified one. It is also interesting that the variation in $k_1$ and $k_2$ over the AcOH-modified catalyst is the same as those previously observed over the $CoCl_2$- and $MnCl_2$-modified catalysts.[2] Taking into consideration the facts that AcOH has the Brönsted acidity and that Co- and $MnCl_2$ have the Lewis acidity, these results can be considered to indicate that the action of acids as modifiers differs from that of bases, especially in the effect on the formation of UA, although the reason is not yet well known. No detailed or quantitative discussion of the variation in the kinetic parameters observed in the present study is possible, since the effect of modifiers on the kinetic parameters is not simple.

If a modifier is adsorbed competitively with the reactants and without any interaction among them, the rate equation can be expressed as:[4]

$$r = k_a b_a C_{UD}/(1+b_a C_{UD})^2 \tag{3}$$

where $k_a$ and $b_a$ denote the apparent rate constant and the adsorption parameter respectively. The definitions of the apparent kinetic parameters are as follows:

$$k_a = k/(1+b_M C_M) \tag{4}$$

$$b_a = b/(1+b_M C_M) \tag{5}$$

where $b_M$ and $C_M$ denote the adsorption parameter and the liquid-phase concentration of a modifier respectively. It can thus be said from Eqs. (4) and (5) that the rate constants and adsorption parameters determined by Eqs. (1) and (2) apparently decrease with the addition of a modifier, provided that there is no interaction between the adsorbed modifier and the reactants. The variation in the kinetic parameters for the formation of SD and SA ($k_1$ and $b_1$) over the AcOH- and $PPh_3$-modified catalysts, therefore, seems to be explainable in terms of the above-described Langmuir-Hinshelwood mechanism.

Both of the adsorption parameters over the AcOH-modified catalyst were found to decrease, even on the first addition of a small amount of AcOH. This indicates that AcOH is adsorbed on the site responsible for the formation of UA as well as on that responsible for the formation of SD and SA. Therefore, the fact that $k_2$ did not change, or even increased, on the first addition of a small amount of acidic modifiers, such as AcOH, $MnCl_2$, and $CoCl_2$, can certainly be considered to be due to an increase in the rate constant, $k$, in Eq. (4). This indicates that the acidic modifiers promote the formation of UA, suggesting that an interaction exists among the adsorbed acidic modifier and adsorbed species responsible for the formation of UA.

---

[4] S. Kishida, C. Ko, and S. Teranishi, *Shokubai*, **11**, 146 (1969).